Study on Effective Adsorption Conditions for Perfluorinated Compounds (PFCs) Removal in Municipal and Industrial Wastewaters in Thailand and Japan

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Abstract

Perfluorinated compounds (PFCs) are a group of synthetic chemical that have been used for a variety of consumer and industrial applications. They are characterized as long, fully fluorinated carbon chains with different functional groups. Nowadays, PFCs are considered as persistent, bio-accumulative, toxic and ubiquitously detected in natural water. Thus, monitoring of releasing sources and effective removal technique are needed to minimize discharging of PFCs into water environment. This research aimed to study effective adsorption conditions for PFCs removal in wastewater. Source of PFCs were monitored both in municipal wastewater and industrial wastewater. Anion exchange resins and granular activated carbon (GAC) were examined for removal of PFCs. The selected resin was used to study on regeneration and reusability. Finally, column experiments were conducted to remove dominant PFCs which were perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in synthetic wastewater and applied in real industrial wastewater.

Source of PFCs contamination in municipal wastewater in developing countries, such as Thailand, is still unavailable. Therefore, Bangkok was selected for studying PFCs contamination in seven municipal wastewater treatment plants (MWWTPs). The investigation was conducted in October to November, 2011. Among seven MWWTPs, Chong Nonsi MWWTPs had the highest concentration of PFCs in final effluent (63.6 ng/L). PFOS and PFOA were predominant PFCs. Long-chain PFCs tended to adsorb on particulate phase more than shorter ones. Moreover, effluent from five industrial wastewater treatment plants (IWWTPs) were also collected in May to June, 2012. The PFCs concentration was found in the range of 62.7 to 660.6 ng/L, which was higher than in municipal wastewater. Thus, industrial activities are the major source of PFCs contamination in the water environment.

Adsorption is an effective technique that is widely used for water and wastewater treatment. Anion exchange resins (PFA300, PFA400, PFA444, Dow Marathon A and

IRA400) and GAC were tested by batch experiments for PFCs adsorption in ultrapure water. The result showed that PFOS was adsorbed onto adsorbents faster than PFOA. PFA300 showed the highest adsorption capacity for both PFOS and PFOA. Next, adsorption capacities of eight PFC onto PFA300 were examined with in single adsorbate condition. Short-chain PFCs showed higher adsorption due to more hydrophilic which was easier to diffuse into the adsorb sites. Mixed PFCs were tested under same experimental condition as single PFC adsorption. The results showed that long-chain PFCs, which have more hydrophobic, were adsorbed higher than shorter ones. Effects of pH, temperature and ionic strength were investigated. The adsorption of PFOS and PFOA onto PFA300 increased with decreasing pH. The maximum adsorption was found at 40°C and amount of PFOA adsorbed was the highest at ionic strength of 0.1 mM NaCl.

PFA300 was also selected for regeneration and reusability. The regeneration studies of PFA300 were conducted using different types of regeneration solutions. PFA300 was successfully regenerated by 5% NaCl in methanol/ultrapure water (7:3) which showed the fastest regeneration rate. The regeneration efficiency of PFA300 exceeded 99%. The regenerated PFA300 was reused as an adsorbent and showed high PFOS removal efficiency for six cycles (more than 97%). Since, PFA300 can be regenerated and reused, resin-based water/wastewater treatment is economical.

Continuous removal of PFOS and PFOA were examined by column experiments. During first run, anion exchange resins and GAC were applied for removal of PFOS (5 μg/L) in column setup. In second run, anion exchange resins, non-ion exchange resin and GAC were tested for removal of PFOA. The breakthrough point was set at 90% removal efficiency. The result showed that PFA300 showed the highest performance for removal of both PFOS and PFOA. In addition, regeneration of PFA300 using solvent washing technique was more economical than thermal regeneration of GAC by approximately 5 times per each cycle.

Since, industries are the major source of PFCs released into water environment, so the removal technique should be applied to minimize the impact of discharging treated

wastewater which contained high concentration of PFCs. Firstly, batch adsorption experiments were carried out using industrial wastewater. PFA300 was used as adsorbent for PFOS and PFOA removal from industrial wastewater. It was found that matrix interferences such as dissolved organic carbon (DOC) influenced on adsorption. Secondly, column adsorption technique was applied in wastewater containing PFOA. Columns were installed at the discharge point from IWWTP. Suitable adsorbent, flow rate and bed volume were studied. Moreover, the optimum conditions of column were applied in PFOS-related industrial wastewater. PFA300 was used in column setup and showed high performance on removal of PFOS and PFOA in industrial wastewater.

Industrial sector is major contributor of PFCs into water environment. Anion exchange resin in column setup successfully removed PFCs from industrial wastewater. In additional, anion exchange resins can be regenerated and reused for water/wastewater treatment. Adsorption technique is economical and practically applied in water/wastewater treatment process. Thus, reduction of PFCs released into water environment can be accomplished using effective adsorption technique.

Keywords

Perfluorinated compounds (PFCs), industrial wastewater, adsorption, regeneration, Japan and Thailand

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Abbreviations

AC	activated carbon
AFFF	aqueous fire-fighting foams
AS	activated sludge
Ave	average
BMA	Bangkok metropolitan administration
DOC	dissolved organics carbon
ESI	electrospray ionization
GAC	granular activated carbon
HCB	hexachlorobenzene
HRT	hydraulic retention time
HPLC	high-performance liquid chromatography-tandem mass spectrometry
IE	industrial estate
IWWTP	industrial wastewater treatment plant
LC	liquid chromatograph
LOD	limits of detection
LOQ	limits of quantification
MS/MS	tandem mass spectrometer
MWWTP	municipal wastewater treatment plant
NOAEL	no observable adverse effect level
NOM	natural organic matter
PBTs	persistent, bioaccumulative and toxic
PCD	pollution control department (Thailand)
PFASs	perfluoroalkyl sulfonates
PFBuS	perfluorobutane sulfonate
PFCAs	perfluorocarboxylates
PFCs	perfluorinated compounds
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFHpA	perfluoroheptanoic acid

PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPA	perfluoropentanoic acid
PFUnDA	perfluoroundecanoic acid
PET	Polyethylene terephthalate
POPs	persistent organic pollutants
PCBs	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	dibenzofurans
PP	polypropylene
RO	reverse osmosis
SRT	sludge retention time
TDS	total dissolved solid
WWTP	wastewater treatment plant

Chapter 1

Introduction

1.1 Research Background

Micro-pollutants have been increasingly considered as an issue in fresh water pollution and contamination. The uses of advanced chemical compounds and high technologies have dramatically released huge amounts of toxic micro-pollutants containing wastewater to environment, especially persistent organic pollutants (POPs) which are persistent, bio-accumulative, and toxic. Twelve POPs consisting of aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), Mirex, Toxaphene, polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) have been identified as the initial POPs in the Stockholm convention (UNEP, 2001). This convention is an international environmental treaty aims to eliminate or restrict the production and use of POPs.

Perfluorinated compounds (PFCs) have emerged as an utmost prioritized micro-pollutant that is creating a disaster in the water environment. PFCs are fully fluorinated of the carbon atom in organic molecules with a terminal sulfonate, carboxylate, or phosphonate groups. PFCs have been used in a variety of consumer products and industrial applications such as polymers, metal plating and cleaning, surfactants, lubricants, pesticides, coating formulations, inks, varnishes, firefighting foam, and stain/water repellents for leather, paper and textiles (Kiss, 1994). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) were dominant compounds in PFCs group and often found in water environment (Ahrens *et al*., 2010). PFOS was recently added to the list of POPs at the Stockholm Convention of Annex B. Furthermore, PFOS and its derivatives are banned by the European Union. However, PFCs have still been detected in water environment. The reason could be due to the substitution of PFOS by other PFCs such as PFBuS (Ritter, 2010).

PFOS and PFOA have been found throughout the world in wastewater, surface water, groundwater and tap water (Fujii *et al*., 2007; Moody and Field, 1999 and Saito *et al*., 2003). High concentrations of these compounds are often found in the effluents of industrial wastewater treatment plants (Lien *et al.,* 2008; Kunacheva *et al*., 2011).

As the conventional wastewater treatment techniques are not sufficient to treat PFOS and PFOA, alternative treatment methods are developed for their removal. Many researches have been done on removal of PFCs by advanced treatment systems such as sonochemical degradations (Moriwaki *et al*., 2005), UV-visible light irradiation (Hori *et al*., 2004) and reverse osmosis and nanofiltration (Tang *et al*., 2006). However, these techniques have some limitations because they require high energy and/or are interfered with by other compounds in the wastewater (Ochoa-Herrera and Sierra-Alvarez, 2008). Adsorption process has been identified as an economical and effective technique to remove pollutants from water and wastewater (Qu *et al*., 2009). Conventional adsorbents such as activated carbons are used by some PFCs manufacturers in order to remove PFCs from wastewater. However, the adsorption capacities of activated carbon are not very high (Ochoa-Herrera and Sierra-Alvarez, 2008; Yu *et al.,* 2009), resulting discharge of PFCs from the treatment system which causes PFCs contamination in water environment.

Polymer resins have been found to be effective material for removal of PFCs from wastewater (Lampert *at al*., 2007). Anion exchange resin can be effective material to remove PFCs because it has high stability (physic-chemical), large adsorption capacity and selectivity to target compound. The most advantage of resin is easy for regeneration and can be reused. Until now, only a few researchers have reported efficiencies of anion exchange resins to remove PFCs in pure water (Deng *et al.,* 2010; Senevirathna *et al.,* 2010; Yu *et al.*, 2009).

In general resins can be regenerated, therefore water and wastewater treatment processes using resins is economical. Generally, anion exchange resins are regenerated by high concentration of NaCl and NaOH. However, Deng *et al.* (2010) reported high concentration of NaCl and NaOH could not desorb PFCs that were adsorbed onto resin.

Therefore, the suitable regeneration solution for adsorbed PFOS onto resin should be studied. Until now, the information of regeneration and reusability of used resin for removal of PFCs are unavailable. Therefore, this report is important for contributing new information to this research topic.

Furthermore, there is lack of information on practical removal of PFCs. Although in general practice, resins are used in column mode, most researches focus only on the batch adsorption mode. Therefore, the results of this study are critical in providing information on PFOS removal from the practicality prospective. Moreover, the column study was conducted at trace PFCs level, which is close to its actual level detected in wastewater.

1.2 Research Objectives

The main objective was to study effective adsorption conditions for PFCs removal in wastewater. To achieve the main objective, specified objectives of this study are established as below:

1. To determine the contaminations of PFCs in MWWTPs and IWWTPs
2. To examine effectiveness of adsorbents on removal of PFCs
3. To study regeneration and reusability of adsorbents
4. To examine continuous PFOS and PFOA removal by column experiments
5. To apply the PFCs removal techniques to industrial wastewater

Based on research backgrounds, to avoid the dispersion of PFCs in the environment and to minimize the subsequent negative effects on living organisms, this study focused on the removal of PFCs in water/wastewater. First, surveys were conducted in municipal wastewater treatment plants (MWWTPs) and industrial wastewater treatment plants (IWWTPs) to investigate PFCs contamination (Chapter 3). Next, adsorption technique was developed for removal of PFCs by batch experiments (Chapter 4). Then regeneration and reusability of adsorbents were studied (Chapter 5). Finally, column studies were conducted to investigate removal efficiency of PFOS and PFOA in both synthetic wastewater and industrial wastewater (Chapter 6 and 7).

This dissertation consists of eight chapters are shown in **Fig. 1.1**.

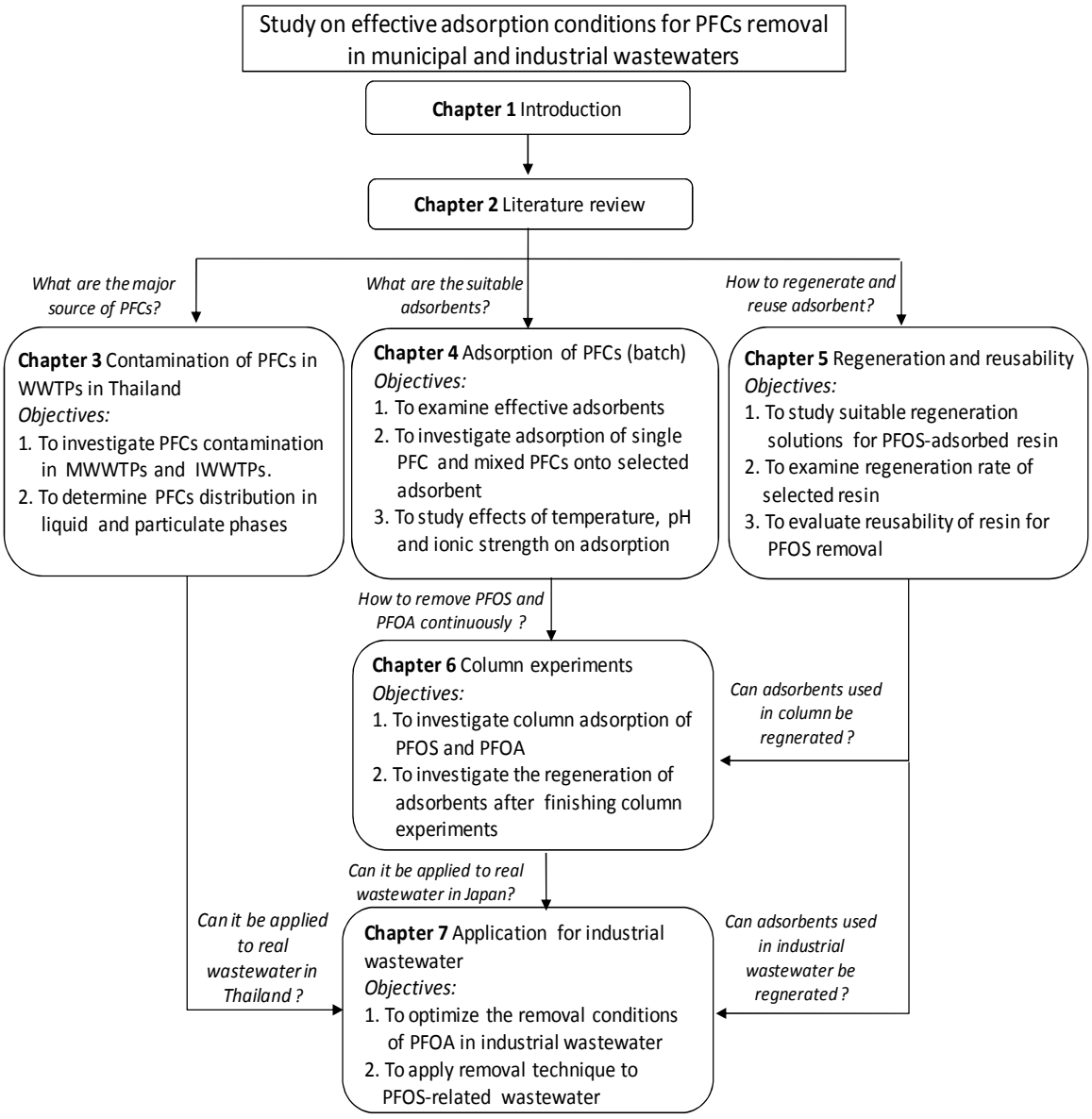


Figure 1.1 Framework of the study

Chapter 2

Literature review

2.1 Introduction of perfluorinated compounds (PFCs)

2.1.1 Properties of PFCs

PFCs are synthetic chemical compounds in which all hydrogen atoms are replaced by fluorine atoms on a carbon chain. They contain at least one different atom or functional group. PFCs can be generated using two methods (i) electro-chemical fluorination (ECF) (3M Company, 1999) and (ii) telomerization-fluorination processes (Brace, 1961).

Carbon-fluorine (C-F) bond in PFCs molecule is the strongest bond in organic chemistry. Their bond is approximately 1.35 angstrom (1.39 Å in fluoromethane), which is shorter than any other carbon-halogen bonds. Since the highest electro negativity of fluorine in all halogens shows the stability (chemically and thermally very stable, resistant to hydrolysis, photolysis, microbial degradation or metabolism) of PFCs, this confers a variety of unique properties to fluorochemicals (3M Company, 1999).

PFCs can be divided into two major popular groups, one is perfluoroalkyl sulfonates (PFASs) and another is perfluorocarboxylates (PFCAs). Their chemical structures are shown in **Table 2.1**. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) have eight carbons and the chemical formulas of PFOS and PFOA are $C_8F_{17}SO_3^-$ and $C_8F_{15}COO^-$, respectively. The functional groups of PFOS and PFOA molecule possess hydrophilic properties and perfluorinated carbon chain possesses hydrophobic properties. These characteristics make PFOS and PFOA unique surfactants, making them suitable for various industrial applications. **Table 2.2** shows physical and chemical properties of PFOS and PFOA.

Table 2.1 Chemical structure of PFCs (PFASs and PFCAs)

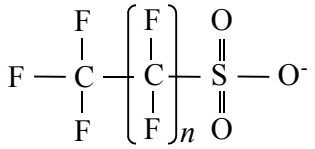
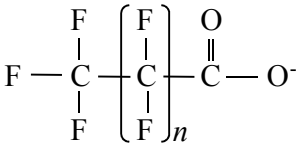
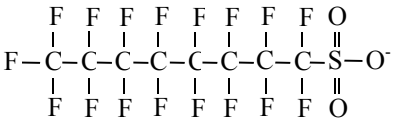
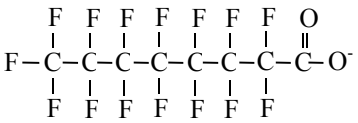
Perfluroalkyl sulfonate (PFASs)	Perflurocarboxylate (PFCAs)
	
$CF_3(CF_2)_nSO_3^-$	$CF_3(CF_2)_nCOO^-$
	
PFOS	PFOA

Table 2.2 Physico-Chemical properties of PFOS and PFOA

Properties	Unit	PFOS	PFOA
CAS No.		1763-23-1	335-67-1
Molecular formula		$C_8F_{17}SO_3H$	$C_8F_{15}O_2H$
No. of carbon		8	8
Molecular weight	g/mol	500	414
Appearance (at normal temperature and pressure)		2.05	1.7
Melting point	°C	≥400	45-50
Boiling point	°C	Not available	189-192
Vapor pressure at 20 °C	mm Hg	2.48 x 10-6	0.017
Solubility in pure water	mg/L	570	3,400
p*Ka*		-3.27	2.5
pH		7-8 (potassium salt of PFOS)	2.6 (at 1 g/L)
Air/water partition coefficient	($Pa.m^3/mol$)	Not available	$< 2 \times 10^{-6}$
Half-life:			
- Human serum	year	3.5	4.8
- Atmospheric	day	114	90
- Water	year	>41 (25 °C)	>92 (25 °C)

Source: USEPA (2002), USEPA (2013) OECD (2002) and Olsen *et al*. (2007)

There are variety of PFCs which are short-chain (C4 - C7), medium-chain carbon (C8), and long-chain (C9 - C12). Basic information of PFCs in this study is shown in **Table 2.3**.

Table 2.3 Basic information of PFCs in this study

PFCs	Abbreviation	Molecular structure
Perfluorobutane sulfonate	PFBuS	$CF_3(CF_2)_3SO_3K$
Perfluorohexane sulfonate	PFHxS	$CF_3(CF_2)_5SO_3Na$
Perfluorooctane sulfonate	PFOS	$CF_3(CF_2)_7SO_3Na$
Prefluorobutanoic acid	PFBA	$CF_3(CF_2)_2COOH$
Perfluoropentanoic acid	PFPeA	$CF_3(CF_2)_3COOH$
Perfluorohexanoic acid	PFHxA	$CF_3(CF_2)_4COOH$
Perfluoroheptanoic acid	PFHpA	$CF_3(CF_2)_5COOH$
Perfluorooctanoic acid	PFOA	$CF_3(CF_2)_6COOH$
Perfluorononanoic acid	PFNA	$CF_3(CF_2)_7COOH$
Perfluorodecanoic acid	PFDA	$CF_3(CF_2)_8COOH$
Perfluoroundecanoic acid	PFUnDA	$CF_3(CF_2)_9COOH$
Perfluorododecanoic acid	PFDoDA	$CF_3(CF_2)_{10}COOH$

2.1.2 Use of PFOS and PFOA

PFCs have unique properties as they are chemically and thermally stable, water and oil repellent; hence used in various industries. PFOS had been used in industries such as stain-resistant coating for fabrics, leather, furniture and carpets, firefighting foam, cleaning products, pesticides, semiconductors, photography, and aviation.

The total amount of PFOS and related compounds used in the USA was estimated to be 3,000 tones. Even though PFOS has been used in industries for many decades, the concerns of PFOS toxic effects were raised in the early 2000s. During the time, 3M Company had decided to phase out production of PFOS-related products. In 2003, they substituted PFOS in their Scotchgard products with shorter carbon chain, namely, PFBuS (perfluorobutane sulphonate). Finally, PFOS was announced as one of new POPs in the Stockholm Convention in 2009.

Table 2.4 Uses of PFOS and its related substances

Group	Uses/Applications	Product	Substances used
1. Surface treatment	1.1 Treatment of fabrics	Apparel/Textiles Fabrics/upholstery Carpets Automotive interiors	FOSE alcohols FOSE silanes FOSE alkoxylates FOSE fatty acid esters FOSE adipates FOSE urethanes FOSE polyesters FOSE acrylates FOSE copolymers
	1.2 Treatment of metal and glass	Metal/Glass	
	1.3 Leather treatment	Leather	As above, including PFOSA amphoterics
	1.4 Mist suppressant Corrosion inhibitors	Metal plating baths	PFOSA, K^+, Li^+, DEA and NH_4^+ salts
2. Paper production	2.1 water/oil/grease/ solvent repellent	Plates and food containers Bags and wraps Folding cartons Containers Carbonless forms Masking papers	FOSE acrylates FOSE copolymers FOSE phosphate esters
3. Performance chemical	3.1 Surfactants	Fire fighting foams Alkaline cleaners Mine and oil well surfactants	PFOSA, K^+, Li^+, DEA and NH_4^+ salts
	3.2 Cleaning agents	Denture cleaners Shampoos Carpet spot cleaners Mould release agents	
	3.3 Waxes and polishes	Emulsifier in wax and floor polishes	
	3.4 Coating	Coating additives	
	3.5 Photography	Antistatic agents for paper, films, photographic plates	FOSA carboxylates
	3.6 Photolithography	Coatings for semiconductors anti-reflective coatings	
	3.7 Pesticides/insecticides	Pesticides active ingredient, Active ingredient for ant bait traps	FOSA amides and PFOSA amines
	3.8 Chemical synthesis	Chemical internidiates	PFOSF, PFOSA, FOSA, FOSE
	3.9 Medical applications	Waterproofing casts/wound dressings	FOSA oxazolidones
	3.10 Hydraulic fluids	Hydraulic fluid agents	

Sources: OECD (2002) (PFOSA: Perfluorooctanesulphonic acid;
FOSA: N-Alkylperfluorooctanesulphoamide; FOSE: N-Alkylperfluorooctanesulphonamidoethnol;
PFOSF: Perfluorooctanesulphonyl fluoride and DEA: Diethanolamine)

Hence, control and monitoring of PFOS synthesis and use in industry have been strict. The use of PFOS in industry is classified into two groups for monitoring, *viz*. acceptable uses and specific exemption. The overview of uses of PFOS and its related substances is shown in **Table 2.4**.

PFOA is primarily applied as a reactive intermediate, while its salt is used as processing aid in synthesis of fluoropolymer such as polytetrafluoroethylene or Teflon®, fluorotelomer alcohol (FTOH). In EU, less than 1,000 tones/year of usage was estimated (OECD, 2005). Many industries have used PFOA in aerospace, automotives, building construction, semiconductors, electronics, textiles, fire-fighting foam and *etc*.

2.1.3 Toxic effects

Acute Effects

PFOS and PFOA are toxic compounds and their acute effects on human have not been studied yet. However, several researches have reported their acute effects in animals. LC_{50} (lethal concentration 50) value used to indicate the concentration that causes lethal effect to 50% of tested animals. Health Protection Agency, HPA (2009) summarized acute effect of PFOS and PFOA as below.

1. Inhalation: Rats were exposed for 1 hour of high PFOS concentrations dust in air (1.9 - 46 mg/L). The LD_{50} for PFOS was 5.2 mg/L and no data is available for PFOA
2. Ingestion: The oral LD_{50} for PFOS in rats was 230 and 270 mg/kg bw for males and females. LD_{50} for PFOA in rats ranged between 430 - 680 mg/kg bw.
3. Dermal: Rabbits were administered with 0.1 g and 0.5 g of PFOS for eye and skin irritation, respectively. PFOA caused mild skin irritation in rabbits.

Chronic Effects

Chronic effect is a dose that delivers adverse effects after exposed to a chemical for a period of time. The chronic effects of PFOS and PFOA on humans have not been well studied. Chronic effects of PFOS and PFOA are shown below.

1. Incidence of bladder cancer and an enhanced risk of neoplasm of the male reproductive and gastrointestinal tract were reported to be associated with PFOS exposure (HPA, 2009).
2. The negative association between birth weight and head circumference of newborn with PFOS and PFOA concentration in cord blood has been reported (Apelberg *et al.*, 2007).

Moreover, risk of gastrointestinal, biliary, reproductive tract, pancreatic cancers were found to increase after repeated exposures of those compounds (HPA, 2009). Large numbers of studies have shown chronic effects of PFOS and PFOA on animals (HPA, 2009). Overall, the critical effects on liver and reproduction system were found in animals and vitro studies. The effects of PFOS and PFOA on tested animals (rat and monkey) by oral exposure are shown in **Table 2.5**.

Table 2.5 Health effects of PFOS and PFOA on tested animals (oral exposure)

PFOS/ PFOA	Tested animals	Dose (mg/kg bw/day)	Duration	Effects
PFOS	Rat	1.4	14 weeks	Increased liver weight
	Rat	1.6	4 weeks	Significantly increased liver weight
	Rat	3	28 days	Increased relative liver and kidney weight and reduced body weight
	Monkey	0.03	26 weeks	Increased liver weight
	Monkey	0.75	26 weeks	Death due to pulmonary inflammation and necrosis
PFOA	Rat (male)	64	90 days	Death
	Rat (female)	76	90 days	Death
	Monkey	20	4 weeks	No clinical signs of toxicity or changes in body weight
	Monkey	30	26 weeks	Weight loss, reduced food consumption, and liver toxicity

Source: Summarized from HPA (2009)

2.1.4 Regulation of PFOS and PFOA

2.1.4.1 Timeline of regulations for PFOS and PFOA

The important events related with PFOS and PFOA are shown in **Table 2.6**.

Table 2.6 Timeline of important events related to PFCs

Year	Orgz./person	Activities
1938	Dr. RJ Plunkett	Discovers Teflon by accident as a failed experiment
1949	DuPont	Introduces Teflon
1951	DuPont	Begins using ammonium perfluorooctanoate, also called C8 to make Teflon
1953	3M	Discovers Scotchgrad by accidental spilling on tennis shoes
1956	3M	Starts to sell Scotchgard Protector
1968	Dr. Taves	Finds two forms of fluoride in human serum
1978	3M	Detect C8 in blood of workers. No shard information outside company
1981	DuPont	Detects C8 in blood of five empolyees
1984	DuPont	Finds tap water near DuPont Works contains 1.5 μg/L PFOA in Lubeck
1986	DuPont	Begin selling Teflon-based Stainmaster to protect carpets
1999	DuPont	Dumps 55000 pounds of PFOA into Ohio River
1999	3M	Becomes aware the PFOS and PFOA
2000	3M	Announces phasing out of production of PFOS and related chemicals
2002	US EPA	Review of data that links C8 to health problems
2002	OECD	Issues hazard assessment of PFOS and its salts
2003	3M	Replaces C8 in Scotchgard with a C4 chemical
2004	CA	Issue exposure to PFOS and related precursors by Health Canada
2005	US EPA	Issues risk assessment of PFOA-related chemicals on human health
2006	US EPA	Initiates 2010/15 PFOA stewardship program
2007	EC	Releases Directive 2006/122/EC
2007	MDH	Sets health based volume of PFOS and PFOA
2007	NJ	Releases PFOA guidance in drinking water
2008	NC	Establied an interim maximum allowable concentration of 2 μg/L of PFOA in drinking water
2009	UNEP	Perfluorooctane sulfonci acid, its salts and perfluorooctane sulfonyl fluoride were selected as new POPs
2009	US EPA	Provisional health advisory of 0.2 μg/L for PFOS and 0.4 ug/L PFOA in drinking water
2009	US EPA	Recommended a residential soil screening level of 6 mg/kg of PFOS and 16 mg/kg for PFOA

Modified from Fluoride Action Network, 2005
Note: CA = Canada, EC = European Commission, MDH= Minnesota Department of Health, NJ = New Jersey and NC = North Carolina

2.1.4.2 Discharge criteria of PFOS and PFOA

Though, PFOS and PFOA were detected at high concentration in environment matrices as well as in human blood, there has been no strict standard and discharging criteria. In developed counties such as USA, England, Canada and Germany, the recommended value of PFOS and PFOA in drinking water is shown in **Table 2.7**.

Table 2.7 Acceptable concentration of PFOS and PFOA in drinking water

State	**PFOS (µg/L)**	**PFOA (µg/L)**
Minnesota	0.2	0.3
New Jersey	NA	0.04
North Carolina	NA	2
Agency		
USEPA	0.2	0.4
UK HPA	0.3	10
Canada	0.3	0.7
German	0.1 (sum of PFOS and PFOA)	

Source: Analytical guidelines for PFCs (2012)

Minnesota Department of Health also recommended 7 µg/L for PFBA and PFBuS in drinking water (MHD, 2007). New Jersey issued the lowest guidance level of 0.04 ng/L of PFOA in drinking water. There is no any guideline or regulation in developing countries. Therefore, PFCs manufacturers have been shifting to developing countries resulting in large distribution of PFCs into water environment.

2.1.5 PFCs and Stockholm Convention

The Stockholm Convention on POPs is a global treaty to protect human health and environment from chemicals that remain intact in the environment for long periods of time, become widely distributed geographically and accumulate in fatty tissue of humans and wildlife (WHO, 2001). This convention was adopted in 2001 and entered

into force in 2004. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland. A separate committee has been established (POPRC) as a subsidiary body to the Stockholm Convention for reviewing new chemicals. PFOS was reviewed by the 4th POPs review committee and they recommended it to be categorized as one of the new POPs. (http://chm.pops.int/Convention/POPsReviewCommittee/hrPOPRCMeetings/POPRC4/POPRC4ReportandDecisions/tabid/450/language/en-US/Default.aspx).

This recommendation was accepted at the fourth meeting of the Conference of the Parties (COP4) to the Stockholm Convention and part III of Annex B was amended. PFOS and its salts were used for the acceptable purposes and specific exemptions. In some application, there are alternatives to PFOS but not for all purposes. For some applications such as photo imaging, semi-conductor or aviation hydraulic fluids, technically feasible alternatives to PFOS are not available to date.

2.2 Alternatives of PFOS and PFOA

PFOS and PFOA were worldwide used and they were regarded as toxic chemical compounds. There are many kinds of chemicals recommended by UNEP which can be alternatives of long chain PFCs (http://www.oecd.org/ehs/pfc/48609862.pdf).

- Shorter-chain perfluoroalkyl sulfonates
- Shorter- shain perfluoroalkyl ketones and ethers
- Polyfluorodialkyl ether sulfonates
- Fluorotelomer and fluorophophates
- Fluorinated co-polymers
- Fluorinated polyethers
- Siloxanes and silicone polymers
- Sulfosuccinates
- Stearamidomethly pyridine chloride
- Polypropylene glycol ether, amines and sulfates

Shorter chain PFCs: Chemical researchers have been trying to replace long-chained PFCs using shorter-chained PFCs because latter compounds are less toxic and bio-accumulative (Xiao *et al*., 2012). PFBuS (C4) derivatives have been identified as alternatives for PFOS (C8) for repellents, cleaning agents, waxes, floor polishes and *etc*. In 2003, 3M replaced C8 in Scotchgard with a C4 chemical. Fluoropolymers were also used as alternatives for monomers because degradation and PFCs release of polymer can be considered negligible. For example, fluorotelomers were used in impregnation for textiles, carpets, paper coatings and floor polishers (Poulsen *et al*., 2005).

Non-fluorine alternatives: Non-fluorine surfactants and polymers can also be used as alternative to long-chained PFCs such as hydrocarbon, siloxanes and silicone polymers. Nowadays the most popular alternatives are C4 and C6 perfluorinated derivatives which are less toxic and bio-accumulative in environment. Silicon and hydrocarbon based surfactants and polymers can substitute PFCs in some applications, but they encounter problems such as low efficiencies or unsatisfactory performances for highly low surface tension (Danish EPA, 2005).

2.3 Distribution of PFOS and PFOA in the environment

PFOS and PFOA and their related-products are released into the environment during their entire life-cycle which includes production process, use of commercial product by consumers and industries or even at landfill, water and wastewater treatment plants.

2.3.1 Surface water

PFCs were detected in surface water (river water, lake, and seawater) and groundwater of both developed and developing countries such as USA, Japan, China, Spain, Hong Kong, Korea and Thailand, especially those close to industrialized areas. The concentrations of PFOS and PFOA are shown in **Table 2.8**.

Table 2.8 PFOS and PFOA levels in water samples

Countries	Types of water	Concentration (ng/L)		References
		PFOS	PFOA	
New York, USA	Surface water	0.8 - 30.0	10.0 - 173.0	Sinclair *et al*. (2006)
Michigan, USA		29.0	36.0	Sinclair *et al*. (2004)
Osaka, Japan		3.0 - 76.0	25.0 - 922.0	Lien (2007)
Decatur, USA		16.8 - 144.0	< 25.0 - 598.0	Hansen *et al*. (2002)
Kyoto area, Japan	River water	< 5.2 - 10.0	7.9 - 110.0	Senthilkumar *et al*. (2007)
China		<LOQ - 88.9	<LOQ-256.0	Wang *et al*. (2013)
Catalonia, Spain		1.0- 9.6	0.8 - 9.6	Sanchez-Avila *et al*. (2010)
North Carolina, USA		30.0 - 132.0	12.6 - 287.0	Nakayama *et al*. (2007)
Onondaga, USA	Lake water	198.0 - 1,090.0	NA	Sinclair *et al*. (2006)
Canadian Arctic		0.9 - 90.0	0.5 - 16.0	Stock *et al*. (2007)
New York, USA		ND – 9.30	3.72 – 15.8	Kim and Kannan (2007)
China		ND - 1.1	4.4 - 15.6	Sun *et al*. (2011)
Osaka, Japan	Tap water	ND - 12.0	0.7 - 40.0	Saito *et al*. (2004)
Naval Air Station Fallon, USA*	Groundwater	NA	ND - 6570	Moody and Field (1999)
Catalonia, Spain	Seawater	0.03-3.90	0.08-1.86	Sanchez-Avila *et al*. (2010)
Coastal area, Japan		<2.5 -59.0	NA	Taniyasu *et al*. (2003)
Wastern Pacific Ocean		0.054 – 0.078	0.136 – 0.142	Yamashita *et al*., (2005)
Atlantic Ocean		0.009 – 0.036	0.160 – 0.338	
Coastal area Korea		0.039 - 2.530	0.239 – 11.350	

Note: * after fire fighting activity, ND= Not detected and NA = Not available

Incomplete treated wastewater was the major source of release of PFOS and PFOA into water environment, especially industrial wastewater which usually contained high concentration of PFCs (Kunacheva, 2009; Sun *et al*., 2011). The dominant PFCs are PFOS and PFOA. Since, the sources of tap water (*i.e.* surface water) and drinking water was contaminated with PFCs, even they contained PFCs due to low performance of treatment processes (Saito *et al.*, 2003; 2004; Skutlarek *et al.*, 2006).

Since, PFOS and PFOA were widely presented in water/wastewater, not only in liquid phase but they were also detected in solid phase. The level of PFOS and PFOA compounds in solid matrices are shown in **Table 2.9**.

Table 2.9 PFOS and PFOA levels in solid matrices

Sample types	Locations	Concentration (µg/kg)		References
		PFOS	PFOA	
Marine sediment (Wet weight)	Charleston harbor area, USA	0.4 ± 0.5	0.2 ± 0.2	Houde *et al* .(2006)
	Ariake Sea, Japan	0.09 – 0.14	0.84 – 1.1	Nakata *et al* .(2006)
River sediment (Dry weight)	Kyoto area, Japan	< 0.33 – 6.4	< 0.1 – 3.9	Senthilkumar *et al* . (2007)
	San Francisco Bay, USA	ND – 1.3	ND – 0.23	Higgins *et al* .(2006)
	Ganges River, India	0.5-14.09	ND- 0.5	Corsolini *et al* . (2012)
Lake sediment (Dry weight)	Dianchi lake, China	0.33	0.21	Xu *et al* . (2013)
Sludge from WWTPs (Dry weight)	San Francisco Bay, USA	14.4 - 2160	ND – 29.4	Higgins *et al* .(2006)
	Kentucky, USA	8.2 – 993	33 - 219	Loganathan *et al* . (2007)
	Georgia, USA	< 2.5 – 77	7.0 – 130	Loganathan *et al* . (2007)
	Korea	3.3 - 54.1	ND - 5.3	Guo *et al* . (2010)
Soil (Dry weight)	USA Osaka, Japan Hokkaido, Japan Mexico	0.61-2.55 0.58 5.15 10.1	1.35-31.7 21.5 1.84 0.76	Strynar *et al.* (2012)

Note: ND = Not detected

In Thailand, 3 rivers were investigated for the PFCs contamination. PFOS and PFOA concentration were detected in Chao Phraya River higher than in Bangpakong River and Tachin River. In additional, PFOS and PFOA were also found to contaminate tap water, drinking water, reservoir and coastal water. The PFOS and PFOA concentration in water environment of Thailand is showed in **Table 2.10**.

The concentration levels in Thai rivers were less than the rivers in Japan, China, and Malaysia. However, PFOS and PFOA loading rate of Chao Phraya River (Thailand) was much higher than Yodo River (Japan), due to higher flow rate (Kunacheva, 2009).

Table 2.10 PFOS and PFOA concentration in water environment in Thailand

Type of water	Concentration (ng/L)	
	PFOS	PFOA
Chao Phraya River	ND-33.06	1.05-36.75
Bangpakong River	< LOQ-2.28	1.73-12.43
Tachin River	ND-3.41	<LOQ-5.35
Tap water	0.18 - 0.45	3.6 - 7.75
Drinking water	0.22 - 0.37	10.55-20.13
Reservior	5.3-572.5	16.7-72.4
Coastal water	4.0-16.4	10.9-101.5
Effluent of industrial wastewater	1.4-130	9.7-937.8

Source: Summarized from Kunacheva (2009)

Effluent of industrial wastewater showed the highest concentration of PFOS and PFOA than other type of water, which can be indicated as their major source. However, usages of PFCs related products also could possible sources of PFCs. The releases depend on the lifespan, use and disposal of the products. There was no information of PFCs concentration in municipal wastewater in Thailand, which could also be a possible source of PFCs in water environment.

The largest municipal wastewater treatment plant is in Bangkok, Thailand. The major source of wastewater in Bangkok was domestic wastewater, accounting 75% of wastewater generated in Bangkok in 1988, while 25% was generated from industrial sources. In 1996, the Pollution Control Department (PCD) estimated industrial wastewater in Bangkok area to be lesser than those estimated by the earlier plan (475,980 m^3/day in 2000 and 167,410 m^3/day in 2016). Tax breaks and duty exemption (the study for the Master Plan for Sewage Sludge Treatment/Disposal and Reclaimed wastewater reuse in Bangkok, 1990) encouraged establishment of industries outside of Bangkok.

Therefore, the major source of wastewater in Bangkok is obviously from the household sector. Municipal wastewater is mostly discharged into a public and combined drainage system without treatment. In the wet season, the drainage system also collects storm water (BMA, 2001). Activated sludge process (AS) is the main treatment system applied in all Bangkok Metropolitan Administration (BMA) central wastewater treatment plants. Discharge of large amount of wastewater in big city as Bangkok, it has high possibility to contribute PFCs into environment which were reported in Chapter 3.

2.3.2 Organism

PFC's have been found to be globally distributed as they were detected in wildlife even in Arctic (Martin *et al.*, 2004b). PFCs were detected in serum of pandas living close to industrial areas (Dai *et al.*, 2006). Contaminations of PFCs in wildlife had different patterns and were caused by multiple sources (Hoff *et al.*, 2005). Olsen *et al.* (2007) reported that PFOS was not metabolized in any species studies and it could bind with protein in blood or assimilate in liver. PFOS were found in most of wildlife, since it has high bioaccumulation factors (BAFs) (Kannan *et al*., 2002). PFOS and PFOA concentration in animals are shown in **Table 2.11**.

2.3.3 Humans

In the past, DuPont and 3M reported that PFOS and PFOA were detected in human serum which led to several organizations conduct surveys in human. PFCs were often detected in human blood, serum and plasma (Hansen *et al.*, 2001) as well as in tissues (Maestri *et al*., 2006). Koreans were estimated to have the highest concentration of PFOS in blood (> 30 ng/mL). Contamination of PFOA was identified in human serum of residents in Osaka and Kyoto, Japan (Harada *et al*., 2004). Blood serum levels in young Danish men were found at level of 10.6 - 53.1 ng/mL for PFOS and 1.9 – 8.6 ng/mL for PFOA (Joensen *et al*., 2009).

Table 2.11 PFOS and PFOA concentrations in some animal species (ng/g wet weight)

Animal type	PFOS	PFOA	References
Zooplankton:			
Cannadian Western Arctic	ND-0.2	ND	Powley *et al*. (2008)
European Arctic	ND-7.41	2.1-4.3	Haukås *et al*. (2007)
Fish (liver)			
Greenland	ND-18	ND	Bossi *et al*. (2005)
USA	9-315	< 1.5-71	Sinclair *et al*. (2006)
Seal (liver)			
Canadian Western Arctic	18-34	ND	Powley *et al*. (2008)
Greenland	ND-67	ND	Bossi *et al*. (2005)
Baltic Sea	9.57-1,444	NA	Kratzer *et al*. (2011)
Bird (liver)			
Faroe Islands	24	ND	Bossi *et al*. (2005)
USA	16-882	ND	Sinclair *et al*. (2006)
Polar Bear (liver)			
Greenland	1,285	< 12	Bossi *et al*. (2005)

Note: ND = Non detected

2.4 PFCs removal techniques

2.4.1 Conventional water and wastewater treatments

Most of water and wastewater treatment used conventional treatment processes which were not sufficient to remove PFCs. Shivakoti *et al*. (2010) reported five WWTPs in Japan and five WWTPs in Thailand, which used conventional activated sludge process and were not been able to remove PFCs effectively. PFOA in effluent was found in higher concentration than in influent by 10 -100% from seven WWTPs in in the United States (Schultz *et al*., 2006). Also in Japan it was found that activated sludge process was ineffective to remove PFOS and PFOA in WWTP (Nozoe *et al*., 2006). In addition, Kunacheva (2009) found that ten industrial WWTPs in Thailand, which used activated sludge process, discharged high concentration of PFCs into water environment. In China, PFOS and PFOA were dominant in municipal WWTPs, were not effectively removed during wastewater treatment (Zhang *et al*., 2013). Furthermore, the possible reason for increase of PFOS and PFOA in effluent could be biodegradation of precursor compounds during activated sludge treatment (Sinclair and Kannan *et al*., 2005; Schultz

et al., 2006). The concentrations of PFOS and PFOA in effluent from municipal WWTPs and industrial WWTPs are showed in **Table 2.12**.

Lien *et al.* (2006) identified the PFOS and PFOA concentration in tap water and surface water in the same area in many countries. The concentrations of PFOS and PFOA in eleven places were not much different between surface and tap water in most samples. This results show that the conventional water treatment process is not effective to treat PFCs.

Table 2.12 PFOS and PFOA concentration in effluent of municipal WWTPs and industrial WWTPs in several countries

Municipal wastewater	PFOS	PFOA	References
Kentucky, USA	8 - 128	120 - 180	Loganathan *et al*. (2007)
New York, USA	6 - 31	130 - 240	Sinclair *et al*. (2006)
Singapore	5 - 16	16 - 150	Yu *et al*. (2009)
German	2 - 8	6 - 11	Becker *et al*. (2008)
Austria	4 - 100	10 - 100	Clara *et al*. (2008)
Korea	0.9-8.9	3.4 - 49.2	Guo *et al*. (2010)
Taiwan	162.7-264.7	25.4-19.3	Lin *et al*. (2010)
Industrial wastewater	PFOS	PFOA	References
New York, USA	4 - 9	67 - 700	Sinclair *et al*. (2006)
Singapore	96 - 460	77 - 1,060	Yu *et al*. (2009)
Japan	640	66	Murakami *et al*. (2009)
Austria	200 - 340	160 - 220	Clara *et al*. (2008)
German	9 - 200	18 - 250	Becker *et al*. (2009)
Taiwan	5663.3	480.3	Lin *et al*. (2010)
Thailand	1.4-130	9.7-937.8	Kunacheva (2009)

Thus, alternative effective treatment techniques are needed. Recently, many researchers have reported several PFCs removal techniques (mostly in aqueous phase) which were useful for developing further effective techniques and applying to the real scale. The removal techniques can be classified as (i) degradation (advanced oxidation process, photolysis and/or photo-catalysis, thermal degradation and sonochemical process) and (ii) separation (membrane filtration and adsorption).

2.4.2 Advanced oxidation process

This process includes the generation of free hydroxyl radicals to react with organic or inorganic compounds via oxidation. The reagents which have been investigated for removal of fluorinated compounds include: O_3, O_3/H_2O_2 and H_2O_2/Fe^{2+} (Fenton's reagent), subcritical water/zero-valent metal and ultrasonic irradiation. Schröder and Meesters (2005) found that some strong reagents like O_3, O_3/H_2O_2 and Fenton's reagent are ineffective for PFOS removal but are able to remove PFOS precursors and, partly, other fluorinated surfactants like fluorinated alkyl-ethoxylates. Hori *et al*. (2006) discovered that sub-critical water is another potential technique for removal of PFOS and other perfluorosulfonates. This method applies subcritical water (350^oC) with zero-valent iron. PFOS molecules are strongly adsorbed on Fe_3O_4 precipitate and further decompose into carbon dioxide and fluorine ions due to oxidation by molecular oxygen in sub-critical water.

2.4.3 Photolysis and photo-catalysis process

Chemical compounds were decomposed by light called photolysis. Photocatalysis refers to decomposition of chemical compounds by catalyst and light. Ultraviolet (UV) is usually applied in water treatment process for disinfection. Hori *et al.* (2004) found that photolysis (220 – 240 nm) degraded PFCAs at 560 mg/L completely. By adding catalyst such as heteropolyacid photocatalyst, the reaction rate of PFOA degradation was highly increased (Hori *et al*., 2004b). Shorter UV wavelength at 185 nm (mercury lamp) or 172 nm (xenon quasi-molecular laser) were found to completely degrade some PFCs at fast rate (Zhang *et al*., 2005b). Sulfate radicals (produced from persulfate ions) reacted with PFCAs and formed positively charged PFCA radicals, which were eventually decomposed to CO_2 and HF in water (Hori *et al*., 2005a). In addition, UV irradiation (310 – 400 nm) successfully decomposed PFOA (300 mg/L) dissolved in perchloric acid within 24 hours by molecular oxygen with catalyst of TiO_2 (Dillert *et al*., 2007).

2.4.4 Thermal degradation process

Yamada *et al*. (2005) conducted experiment under conditions of typical combustion in municipal incinerator with an average temperature of 1000°C and excess amount of air supplied for 2 seconds. The results showed that polyester/cellulose fabric treated with fluorotelomer-based acrylic polymer destroyed PFOA to non-detectable amount.

2.4.5 Sonochemical process

Sonochemical decomposition is degradation reaction that requires sonic wave catalyzes. The ultrasound type has been successfully applied in this process for wastewater treatment. This reaction can decompose PFOS yielding PFOA which is further decomposed to less toxic compounds. Moriwaki *et al*. (2005) degraded PFOS and PFOA under argon atmosphere and the half – life times were very small about 43 and 22 min, respectively. Cheng *et al.* (2008) and Vectis *et al*. (2009) have also evaluated the use of sonochemical degradation to effectively treat PFOS and PFOA in ground water.

2.4.6 Membrane filtration

This process separates target compound between two fractions (permeate and retentate). Reverse osmosis (OR) membrane were found to be effective with 99% rejection of PFOS at concentration of 0.5 - 1,500 mg/L (Tang *et al*., 2006). The membrane flux decreased when PFOS concentration increased.

Nano-filtration membranes have been investigated for PFOS removal and had 90-99% removal efficiency (Tang *et al*., 2007). The improvement of PFOS rejection was observed with mild reduction of flux at longer filtration times. Rattanaudom (2011) found that TS80 (NF membrane) have high rejection percentage, more than 98% of PFOS and PFOA. XN45 (another NF), UE10 and UA50 (two UF membranes) demonstrated 44 - 86% of compounds removal, in which PFOS removal was higher than that of PFOA. **Table 2.13** shows removal of PFOS and PFOA by different techniques

Table 2.13 Removal of PFOS and PFOA by different technologies

Processes	Methods	Target PFCs	Conc. (mg/L)	Removal (%)	By products	Time (hr)
Oxidation	Subcritical water, iron	PFOS	0.46 - 1.86	85 - 96	CO_2 and HF	6
Photolysis/ Photocatalysis	UV, O_2	PFOA	560	90	PFCA(C2-C7)	73
	UV, catalyst	PFOA	140 - 1400	100	CO_2 and HF	24
	UV, persulfate	PFOA	560	100	CO_2 and HF	4
	UV	PFOS & PFOA	0.02	60 - 80	PFCA	24
Sonochemical	Sonic wave, argon atmosphere	PFOS & PFOA	NA	100	Short C- chain	1.4 0.7
Membrane filtration	Reverse osmosis	PFOS	0.5 - 1500	> 99	NA	> 96
	Nanofiltration	PFOS	10	> 99	NA	> 96

Note: NA = Not available
Source: Schröder and Meesters (2005), Moriwaki *et al*. (2005) Tang *et al*. (2007) and Tang *et al*. (2006)

2.4.7Adsorption

More than 90% of PFOS and PFOA can be removed by activated carbon (AC) (Qiu, 2007). The co-existence of natural organic matter (NOM) and carbon fouling had inverse effect on PFCs adsorption, especially for long chain compounds. The fouling had predominant effect on adsorption, rather than existence of NOM. Moreover, the pre-washing of AC could affect rate of adsorption. The pre-washing with acid solution showed faster rate adsorption than base solution because it developed positive charge on AC surface that readily bonded with anion PFCs molecule.

The feasibility study of using powder activated carbon (PAC), granular activated carbon (GAC) and anion-exchange resin (AI400) to remove PFOS and PFOA found that the sorption isotherm of GAC had the lowest sorption capacity for both PFOS and PFOA while, PAC and AI400 showed the highest sorption capacity of 1.04 mmol/g and 2.92 mmol/g of PFOS and PFOA respectively (Yu *et al*., 2009).

GAC has already been applied in industry based on excellent result from lab analysis. However, the decreased efficiency and some operational problems have been demonstrated in industrial application. For example, 3M Cottage Grove facility USA

applied pilot-scale of GAC before effluent from secondary treatment plant discharging to Mississippi River. The aim was to treat all organic contaminants including PFOA. The results showed that it removed more than 99% of PFOA. However, very fast breakthrough period of GAC was observed leading to frequently regeneration of adsorbent.

Senevirathna *et al*. (2010) studied the adsorption of PFOS by using granular activated carbon, ion-exchange polymers and non-ion exchange polymers. GAC and ion exchange polymers reached the equilibrium concentration faster than non-ion exchange. The sorption capacity at 1 µg/L equilibrium concentration decreased from ion exchange polymer, non-ion exchange polymer and GAC respectively. Adsorption isotherm and adsorption kinetics indicated that non-ion exchange (XAD4) and ion exchange polymer (Dow Marathon A) were recommended to eliminate PFOS at ng/L equilibrium concentration. Moreover, column test found that XAD4 removed 99.99% of PFOS (10 µg/L) with 23,000 bed volumes at 15 mL/min flow rate (0.75 bed volume/min).

Ion exchange involves the replacement of an ion in the aqueous phase for an ion in a solid phase. The most widespread use of ion exchange process is in domestic water softening for reducing hardness. This process has been used in water reclamation applications for removal of nitrogen, heavy metals and dissolved compounds. Ion exchange was suggested to be better technology for treatment of PFOS/PFOA in wastewater. The suitable type of resin (A-714) demonstrated more than 99.5% of both PFOS and PFOA removal (Lampert *et al*., 2007).

There are various kinds of adsorbents which were tested for removal of PFOS and PFOA as shown in **Table 2.14**.

Table 2.14 Adsorption of PFOS and PFOA onto different types of adsorbents

Adsorbents	Target PFCs	Conc. (mg/L)	K_f	n	R^2
GAC Calgon F400[1]	PFOS	15-150	60.9	0.29	0.97
	PFOA	15-150	11.8	0.44	0.96
	PFBuS	15-150	9.3	0.46	0.96
NaY80 zeolite[1]	PFOS	15-150	31.8	0.34	0.99
Sludge[1]	PFOS	15-150	1.0	1.01	0.98
PAC[2]	PFOA	5 - 40	24.2	2.22	0.96
Char (W400)[3]	PFOS	1 - 500	5.2	0.49	0.99
Char (M400)[3]	PFOS	1 - 500	7.3	0.49	0.99
Ash (MA)[3]	PFOS	1 - 500	26.8	0.57	0.95
Carbnon nanotube (SMCNT)[3]	PFOS	1 - 500	122.0	0.32	0.99
Carbnon nanotube (MWCNT10)[3]	PFOS	1 - 500	47.1	0.44	0.99
Carbnon nanotube (MWCNT50)[3]	PFOS	1 - 500	14.9	0.57	0.96

Source: [1]Ochoa-Herrera and Sierra-Alvarez (2008), [2]Qu *et al*. (2009) and [3]Chen *et al*. (2011)

Chapter 3

Perfluorinated compounds (PFCs) contamination in municipal wastewater and industrial wastewaters

3.1 Introduction

Wastewater is considered to be the major source of PFCs contamination. Generally, high concentrations of PFCs were detected in industrial wastewater. However, several countries have been reported PFCs contamination in municipal wastewater. PFCs contamination in municipal wastewater came from household activities such as cleaning carpets by surface treatment products, use of personal care products and *etc*. Guo *et al*. (2010) found PFOA was dominant in wastewater from 2.3 – 615 ng/L and 3.4 – 591 ng/L in influent and effluent wastewater respectively. Ahrens *et al*. (2009) investigated effluent of WWTPs and surface waters of the River Elbe found that PFCs concentrations of the river water ranged from 7.6 to 26.4 ng/L, whereas PFCs concentrations of WWTP effluents was approximately 5 - 10 times higher (30.5 - 266.3 ng/L). WWTPs seem to be ineffective for removing PFCs from wastewater hence they are potential sources of releasing PFCs into the river body.

In Thailand, only ten industrial wastewater treatment plants (IWWTPs) have been reported for the high concentration of PFCs in the effluent (Kunacheva 2010), however, there are many IWWTPs which are the possible source of PFCs contamination. In addition, no studies have been done on PFCs contamination in municipal wastewater treatment plants (MWWTPs). As economically booming megacities have high possibility to discharge PFCs along with household sewage, Bangkok, a megacity of Asia was selected for studying PFCs contamination in seven MWWTPs. The survey of WWTPs in Thailand gave important information required to understand the performance of WWTPs for removing PFCs and the state of their contamination in

water environment and also can be used for developing a suitable removal technique for wastewater in Thailand.

3.2 Objectives

The main objective of this chapter was to determine the overall performance of WWTPs on removal of PFCs. Specific objectives of this study are shown as follows.

1. To investigate PFCs contamination in municipal and industrial wastewater
2. To understand the behavior of PFCs distribution in liquid and particulate phases during the wastewater treatment processes
3. To study the distribution pattern of PFCs in WWTPs

3.3 Sampling site information

3.3.1 MWWTPs site information

There are seven MWWTPs in Bangkok. They are operated by BMA namely as Jatujak, Dindaeng, Rattanakosin, Si Phraya, Chong Nonsi, Thoong kru, and Nongkham WWTPs. The total capacity is 992,000 m^3/d (approximately 40 % of total generated wastewater in Bangkok) and the total service area is 191.7 km^2 (about 12.22% of the total area in Bangkok). The conventional wastewater treatment processes (activated sludge) were applied in all MWWTPs. The location of seven MWWTPs is shown in **Fig. 3.1**. General information of each WWTP and sampling date was shown in **Table 3.1**.

3.3.2 IWWTPs site information

Five industrial estates (IEs) were selected from 38 IEs, in Thailand. These IEs have a possibility of PFCs discharged from production processes, but PFCs contamination in those five industrial estates have not been studied yet. Each IE receives wastewater from various types of industries such as electronics, chemical, paper, plastic, glass, food packaging, and automobile. Uses of PFCs in production processes have potential to be released from wastewater of those industries. Activated sludge process is the main

treatment system applied in all IWWTPs. Only IE5, wastewater were further treated by sand filtration and GAC filtration before discharging. The location of each industrial estate is shown in **Fig. 3.2**.

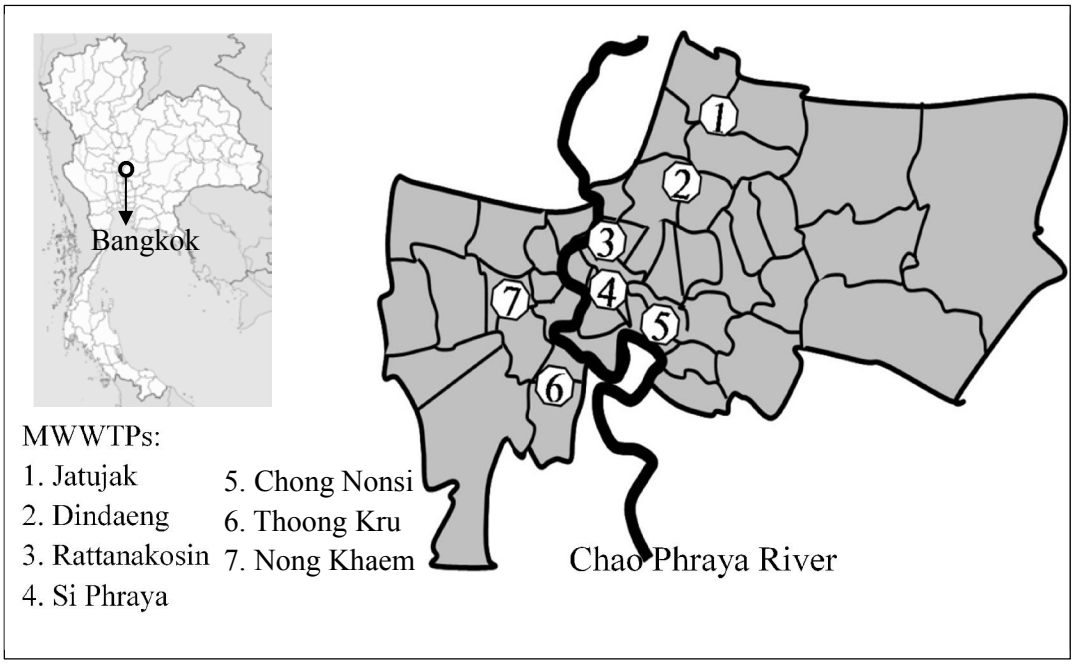


Figure 3.1 Location of seven MWWTPs in Bangkok, Thailand

Table 3.1 General information and sampling date of MWWTPs

Sampling date	MWWTPs	Flow rate (m^3/d)	Service area (km^2)	Service population
10/19/2011	Jatujak (JJ)	150,000	33.4	432,500
10/19/2011	Dindang (DD)	350,000	37	1,080,000
10/20/2011	Rattanakosin (RK)	40,000	4.1	70,000
10/20/2011	Si Phraya (SP)	30,000	2.7	120,000
10/21/2011	Chong Nonsi (CN)	200,000	28.5	580,000
10/21/2011	Thoong Kru (TK)	65,000	42	177,000
10/25/2011	Nong Kheam (NK)	157,000	44	520,000
	Total	**992,000**	**191.4**	**2,978,500**

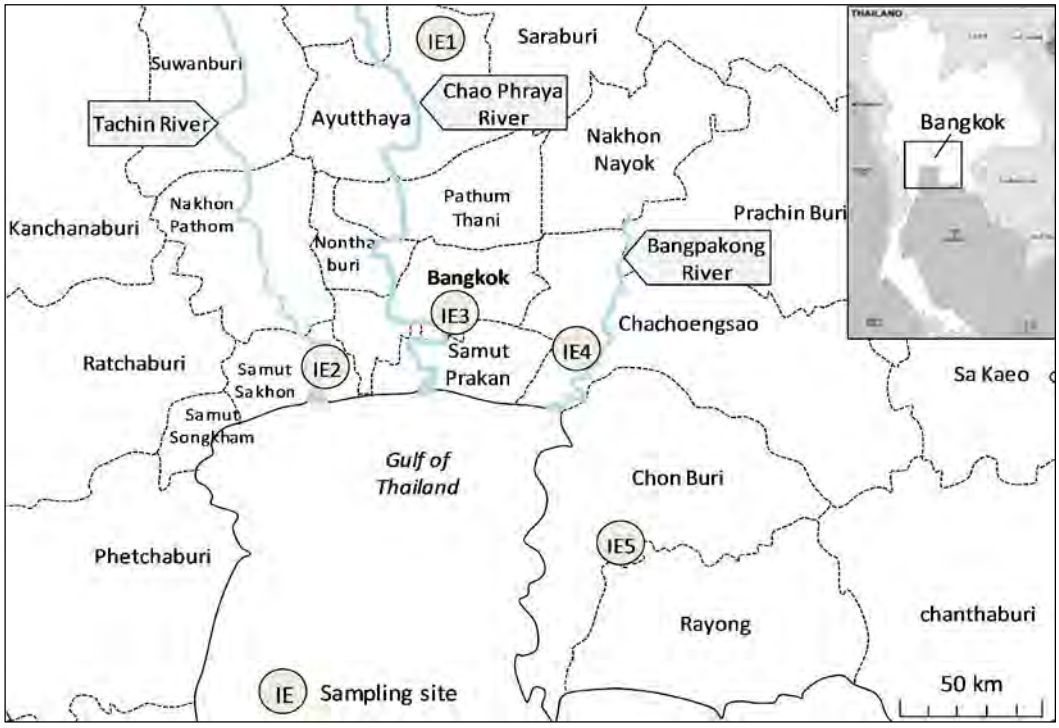


Figure 3.2 Industrial estates sampling location in Thailand

All industries discharge their wastewater into the central WWTP of each industrial estate. Wastewater of each industry is required to meet the criteria of the central WWTP such as BOD < 500 mg/L, COD < 750 mg/L, surfactants (< 30 mg/L) and other parameters (IEAT, 1988). PFCs also were included in 30 mg/L of surfactants. However, 30 mg/L range is much higher than trace levels of ng/L or µg/L. The general information of each industrial estate is shown in **Table 3.2**.

Table 3.2 General information and sampling date of IWWTPs

Sampling date	IWWTPs	No. of industrial	Flow rate (m^3/d)	Wastewater treatment technology
5/18/2012	IE1	48	6,000	AS
5/22/2012	IE2	108	21,000	AS
5/23/2012	IE3	72	10,500	AS
5/24/2012	IE4	149	15,600	AS
6/11/2012	IE5	47	4,750	AS + sand and GAC filtration

Note: AS is activated sludge and GAC is granular activated carbon

3.4 Methodology

3.4.1 Wastewater sampling of WWTPs

Wastewater samples were collected from treatment processes (influent, aeration tank, secondary clarifier and effluent) of each WWTP to investigate the PFCs contamination using grab sampling technique. Tap water was measured to know the background level of PFCs in each MWWTP. The sample from each sampling point was divided into two samples (n = 2). Samples were placed in new 1.5 L narrow-neck polyethlylene terephthalate (PET) bottles. All bottles were washed with methanol, followed by ultrapure water and dried prior to use.

Sample collection of MWWTPs was held in October – November, 2011. For industrial estates, wastewater samples (Tap, influent and effluent) were collected during May – June, 2012. Detailed information was shown in the **Table 3.3**.

Table 3.3 Sampling site information of WWTPs

WWTPs	Date	Site	Detail of sampling	Sampling points
MWWTPs	10/19/2011	JJ	Tap, Inf, Ae, SC, and Eff.	5
	10/19/2011	DD	Tap, Inf, Ae, SC, and Eff.	5
	10/20/2011	RK	Tap, Inf, Ae, SC, and Eff.	5
	10/20/2011	SP	Tap, Inf, Ae, SC, and Eff.	5
	10/21/2011	CN	Tap, Inf, Ae, SC, and Eff.	5
	10/21/2011	TK	Tap, Inf, Ae, SC, and Eff.	5
	10/25/2011	NK	Tap, Inf, Ae, SC, and Eff.	5
IWWTPs	5/18/2012	IE1	Tap, Inf, and Eff.	3
	5/22/2012	IE2	Tap, Inf, and Eff.	3
	5/23/2012	IE3	Tap, Inf, and Eff.	3
	5/24/2012	IE4	Tap, Inf, and Eff.	3
	6/11/2012	IE5	Tap, Inf, and Eff.	3

Note: Tap = Tap water, Inf = Influent, Ae = Aeration tank, SC = Secondary clarifier, Eff = Effluent

3.4.2 Chemicals and reagent

The eleven PFCs were selected as target chemicals, and their stock solutions were prepared by mixing three perfluoroalkyl sulfonates (PFASs) and eight perfluoroalkyl carboxylates (PFCAs) into acetonitrile (LC/MS grade) and storing in polypropylene (PP) bottle at 4°C. The stock solutions were diluted at different concentrations by 40% acetonitrile and used as PFCs standard. PFC internal standards were MPFHxA, MPFOA, MPFDA and MPFOS which prepared similar as PFCs standard. All target PFCs and surrogate standards are shown in **Table 3.4**.

3.4.3 Pre-treatment and extraction

All filtration material was pre-washed with methanol and dried at room temperature. Samples were filtered through dry GF/B filter papers (1 μm, Whatman, Japan), which were washed with methanol and dried. The samples were separated to analyze PFCs in liquid and particulate phases.

Liquid phase: Sample (500 mL) was concentrated into two cartridges in order to enhance recovery of PFCs. The samples were passed through PresepC-Agri (C_{18}) cartridge (Wako, Japan) connected inline with Oasis®HLB (Water, Japan). Both cartridges were pre-conditioned by 10 mL of methanol and 20 mL of ultrapure water, manually. The concentrator pump was pre-washed with methanol for 5 min at 5 mL/min followed by ultrapure water for 15 min at 10 mL/min before concentrating each sample. Filtrated samples were loaded into two cartridges at 5 mL/min.

The above procedures were done in Thailand and all cartridges were brought back to Japan for further analysis. Cartridges were dried in a vacuum manifold (Water, USA) for two hours. Target compounds in dried cartridges were eluted by 2 mL methanol (LC/MS grade) followed by 2 mL of acetonitrile into PP tube. Then, they were evaporated until dried by nitrogen gas and reconstituted with 1 mL of 40% acetonitrile in ultrapure water, then analyzed by HPLC-MS/MS.

Particulate phase: Filter paper of separate solid content from each sample was used for PFCs analysis in particulate phase. Each filter paper was placed into 15 mL PP tube, 5 mL of methanol was added, and shaken at 120 rpm for 30 min. Extracted sample was separated into another PP tube and the extraction processes were conducted 2 times. Final extracted sample (10 mL) was passed through ENVI-Carb cartridge (Supelco, USA), which was cleaned up by 4 mL of methanol in advance. Then, eluent solution was dried by nitrogen gas and reconstituted by 40% acetonitrile in ultrapure water (Suzuki *et al*., 2011).

3.4.4 Analytical technique by HPLC-MS/MS

Separation of PFCs was performed by using Agilent 1200SL high performance liquid chromatography (HPLC), (Agilent, Japan). Ten µL of extracted sample was injected to a 2.1 x 100 mm (5 µm) Agilent Eclipse XDB-C18 column. Mobile phase consists of (A) 5 mM ammonium acetate in ultrapure water (LC/MS grade) and (B) 100% acetonitrile (LC/MS grade). At a flow rate of 0.25 mL/min, separation process began with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then went to 70% (B) at 16.6, held at 70% (B) for 3.4 min, then went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then each sample. The mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ion was monitored by using multiple reactions monitoring (MRM) mode.

Calibration curves for quantification, consisting of six points range from 0.05 to 10 µg/L. The determination coefficient (R^2) of the linear calibration curve was more than 0.99. Limit of detection (*LOD*) was defined as the concentration with signal to noise ration (*S/N*) 3:1. Limit of quantification (*LOQ*) was defined as 10:1 of *S/N*, was used for quantifying analytes. The analysis was replicated on all samples and the coefficients of variations (*CV*) of concentrations were below 20%. The recovery percentages were calculated by spiking PFCs standards into samples. For liquid phase samples, standards were spiked before loading into cartridges, while particulate samples were spiked standards before extraction process.

Table 3.4 Analytical parameters of analyzed PFCs by HPLC-MS/MS

Compounds	Abbreviation	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE (eV)	Retention time (min)	*LOD* (ng/L)	*LOQ* (ng/L)
Perfluorobutane sulfonate	PFBuS	299	80	55	2.7	0.03	0.11
Perfluorohexane sulfonate	PFHxS	399	80	55	7.9	0.04	0.12
Perfluorooctane sulfonate	PFOS	499	80	55	13.8	0.04	0.16
Perfluoropentanoic acid	PFPA	263	219	5	1.9	0.08	0.20
Perfluorohexanoic acid	PFHxA	313	269	5	2.8	0.04	0.08
Perfluoroheptanoic acid	PFHpA	363	319	5	4.7	0.04	0.12
Perfluorooctanoic acid	PFOA	413	369	5	7.2	0.04	0.12
Perfluorononanoic acid	PFNA	463	419	5	9.9	0.04	0.08
Perfluorodecanoic acid	PFDA	513	469	5	12.7	0.04	0.16
Perfluoroundecanoic acid	PFUnDA	563	519	5	15.4	0.28	0.88
Perfluorododecanoic acid	PFDoDA	613	569	5	18.0	0.28	0.88
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	MPFHxA	315	271	5	2.8	0.04	0.08
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	MPFOA	417	373	5	7.2	0.04	0.12
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	MPFDA	515	471	5	12.7	0.04	0.12
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]-octanesulfonate	MPFOS	503	80	55	13.8	0.04	0.16

Note: CE = Collision Energy
LOD = Limit of Detection
LOQ = Limit of Quantification

Table 3.5 Analytical recovery percentage based on spiked PFCs in liquid and particulate phases

Phases	PFBuS	PFHxS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Liquid	77	92	103	89	91	103	93	98	96	86	89
SD	1.9	0.3	4.0	0.1	0.1	1.8	0.8	1.7	1.0	2.7	0.7
Particulate	79	91	95	92	89	98	94	101	100	94	93
SD	2.5	1.3	1.7	0.5	1.9	0.8	1.0	1.4	0.3	0.6	3.5

The extraction recoveries of PFCs were determined from the samples as shown in **Table 3.5** for quantification. The recoveries percentages were calculated as following equation.

$$\%\ Recovery = \frac{(spiked\ sample\ conc.) - (non\ spiked\ sample\ conc.)}{Known\ spike\ added\ conc.}\ x\ 100$$

The recoveries were calculated on the basis of detected spiked concentration in both liquid and particulate phase samples. Recoveries were different, depending on the alkyl

chain length and type of functional group of each PFC. In addition, recovery varied indicating matrix effects on recovery, which is one of the issues in PFCs analysis. Recovery percentages of PFCs standard were in the range of 77% to 103% and most of PFCs were more than 90% in both liquid and particulate phases.

In order to confirm that the recoveries are not affected due to instrument error, the responses of internal standards are added just before the injection of samples into HPLC-MS/MS. The recoveries of internal standard are 94% for MPFHxA, 102% for MPFOA, 100% for MPFDA and 99% for MPFOS.

The recoveries results confirmed that matrices in wastewater samples could possibly compete with PFCs in solid phase extraction (SPE) process for adsorption onto cartridge as well as human errors, but they may not be affecting ionization at electrospray mass spectrometry unit to lager extent.

3.5 Results and discussion

3.5.1 PFCs concentration in municipal wastewater

Several types of PFCs were found in most samples. PFCs concentration in influent (n = 14) and effluent (n = 14) of seven MWWTPs are shown in **Table 3.6**. Tap water samples were also collected to identify the background of PFCs level. The total PFCs concentration in tap water was found at 5.4 ng/L, which was lower than the PFCs concentration in influent and effluent. The total PFCs concentration in influents ranged from 9.4 to 18.4 ng/L while PFCs concentration in the effluent were found higher than the influent ranged from 12.7 to 63.6 ng/L. Among seven MWWTPs, Chong Nonsi (63.6 ng/L) had the highest PFCs concentration in effluent followed by Jatujak (37.2 ng/L), Nong Khaem (29.5), Din Daeng (28.8 ng/L), Si Phraya (24.1 ng/L), Rattanakosin (20.9 ng/L) and Throong Kru (12.7 ng/L), respectively. PFOS and PFOA were predominant and their concentrations were high in both influent and effluent.

The concentration levels of other PFCs were mostly lower than PFOS and PFOA. The concentrations of PFASs (C4, C6, and C8) in effluents were found that PFOS (2.6 to 9.3 ng/L) had the highest concentration in all MWWTPs followed by PFBuS (0.4 – 8.5 ng/L) and PFHxS (0.1 – 6.5 ng/L). Similar results were reported from effluent of a MWWTP in Germany (Ahrens *et al*., 2009). Lange *et al*., 2007 reported that increase of short carbon-chain PFCs as PFBuS concentration in wastewater was due to substitution for PFOS.

For PFCAs, PFOA was the dominant compound, found in higher concentration (2.2 to 7.4 ng/L) in most effluent samples. Shorter carbon-chain PFCs such as PFPeA (1.3 – 5.7 ng/L), PFHxA (2.5 – 5.1 ng/L), and PFHpA (0.8 – 6.8 ng/L) had higher concentrations than longer carbon-chain PFCs such as PFNA (0.4 – 6.5 ng/L) and PFDA (0.8 – 5.3 ng/L). PFUnDA and PFDoDA were not detected in most of samples, except in effluent from Chong Nonsi MWWTPs. Previous studies have reported that perfluoroalkyl carboxylates are produced by biodegradation products of fluorotelomer alcohols (FTOHs) in the activated sludge process (Wang *et al*., 2005). Thus, the biodegradation of precursor compounds during activated sludge process is also a likely source of perfluoroalkyl carboxylates in effluent.

Table 3.6 Concentrations of PFCs (ng/L) in influent and effluent from seven MWWTPs in Bangkok

	Jatujak			Din Daeng			Rattanakosin			Si Phraya			Chong Nonsi			Thoong Kru			Nong Khaem			Ave.
	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Inf	Eff	Eff/Inf	Eff/Inf
PFBuS	1.4	2.3	1.7	1.2	2.6	2.1	0.8	1.8	2.4	0.6	1.9	2.2	1.1	8.5	5.7	1.0	0.4	0.4	1.0	1.4	1.4	2.3
PFHxS	2.2	2.8	1.3	1.1	2.6	2.4	0.5	0.1	1.3	0.9	1.2	2.1	1.4	6.5	5.9	1.0	0.2	0.2	1.3	1.2	0.9	2.0
PFOS	5.6	9.3	1.7	4.0	4.4	1.1	3.3	6.4	2.0	3.4	3.7	1.1	2.7	9.0	3.3	3.8	2.6	0.7	3.5	4.8	1.3	1.6
PFPeA	1.6	5.7	3.5	1.5	2.7	1.8	1.8	2.2	1.2	2.4	1.6	0.7	1.4	1.3	0.9	1.7	2.8	1.6	2.1	4.4	2.1	1.7
PFHxA	1.4	5.1	3.7	0.8	3.9	4.8	0.6	3.2	5.9	1.2	3.4	2.8	1.0	4.0	4.1	0.9	2.5	2.7	1.5	4.2	2.8	3.8
PFHpA	1.2	1.8	1.5	0.5	2.6	4.8	0.4	1.1	3.3	1.1	5.2	4.8	0.5	6.8	14.4	0.9	0.8	0.9	1.8	2.9	1.6	4.5
PFOA	4.4	6.7	1.5	2.3	6.9	3.0	1.5	3.4	2.3	1.8	5.0	2.8	1.8	6.7	3.8	2.1	2.2	1.0	5.4	7.4	1.4	2.3
PFNA	0.4	1.2	3.4	0.4	1.7	4.1	0.6	1.0	1.8	0.5	1.1	2.3	0.4	6.5	17.6	0.5	0.4	0.7	0.9	1.6	1.7	4.5
PFDA	0.3	2.3	7.6	0.2	1.6	9.4	0.2	1.0	5.4	0.8	0.9	1.1	0.2	5.3	21.9	0.2	0.8	3.1	0.4	1.8	4.8	7.6
PFUnDA	ND	ND	–	ND	ND	-	ND	ND	-	ND	ND	-	ND	4.7	-	ND	ND	-	ND	ND	-	-
PFDoDA	ND	ND	–	ND	ND	-	ND	ND	-	ND	ND	-	ND	4.2	-	ND	ND	-	ND	ND	-	-
∑PFCs	18.4	37.2	2.0	12.0	28.8	2.4	9.4	20.9	2.2	12.7	24.1	1.9	10.6	63.6	6.0	12.2	12.7	1.0	18.0	29.5	1.6	2.5

Note: Inf = Influent, Eff = Effluent, ND = Not detect, Ave = average

Shorter carbon-chain PFCs in municipal effluent wastewater were detected at higher concentrations than longer carbon-chain ones (Guo *et al*., 2010). The comparison of PFCs concentration in influent and effluent showed that total PFC concentrations

increased in effluents approximately 2.5 times. The concentration of PFOS and PFOA were found to be higher in effluent than in influent, which describes that both compounds can also be generated through degradation of their precursors in the treatment processes (Loganathan *et al*., 2007). PFCs composition profile in effluent of each MWWTP was shown in **Fig. 3.3**.

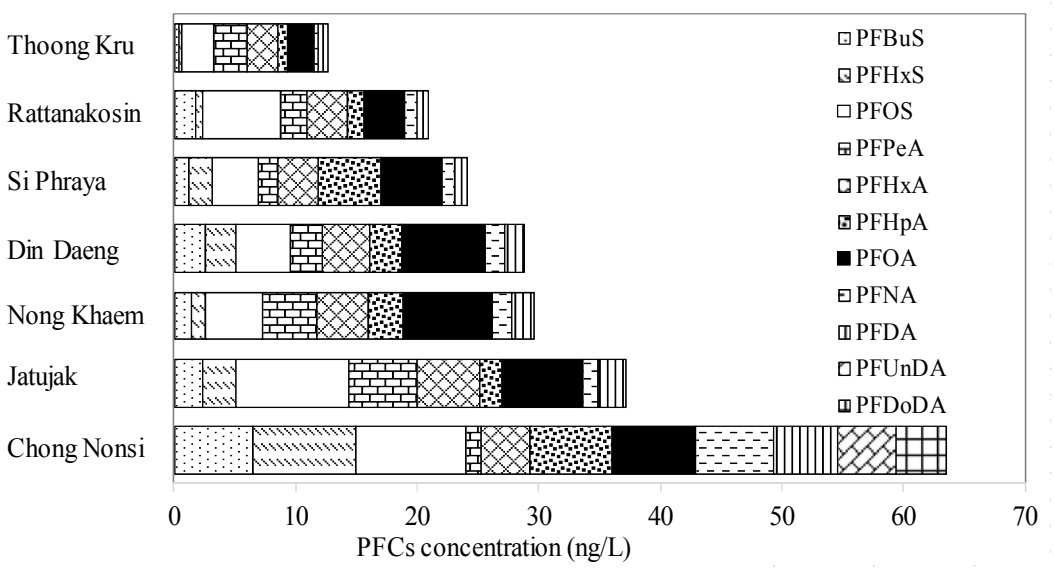


Figure 3.3 Profile of PFCs concentrations in effluent of each MWWTP in Bangkok

Overall, PFOS and PFOA were predominant in all effluent MWWTPs. PFCs concentration at Chong Nonsi was higher than others in 2 - 6 times. Since PFCs in municipal wastewater were detected, the current wastewater treatment processes were not been able to remove PFCs completely. PFCs have been used in several products include protective coatings for food packaging, textiles, carpets, paper, coats, fabrics, leather and non-stick cooking material (Giesy and Kannan, 2002). Daily domestic activities using PFCs containing products could be possible source of PFCs in MWWTP. Therefore, MWWTPs have potential to be one of the sources of PFCs contamination in water environment.

3.5.2 PFCs distribution in municipal wastewater treatment processes and their removal

Earlier it was mentioned that PFCs were detected in most effluent samples. Therefore, the performance of municipal wastewater treatment processes needs to be investigated. **Figure 3.4** shows the comparison of PFCs concentration at influent, aeration, secondary clarifier, and final effluent in both liquid and particulate phases.

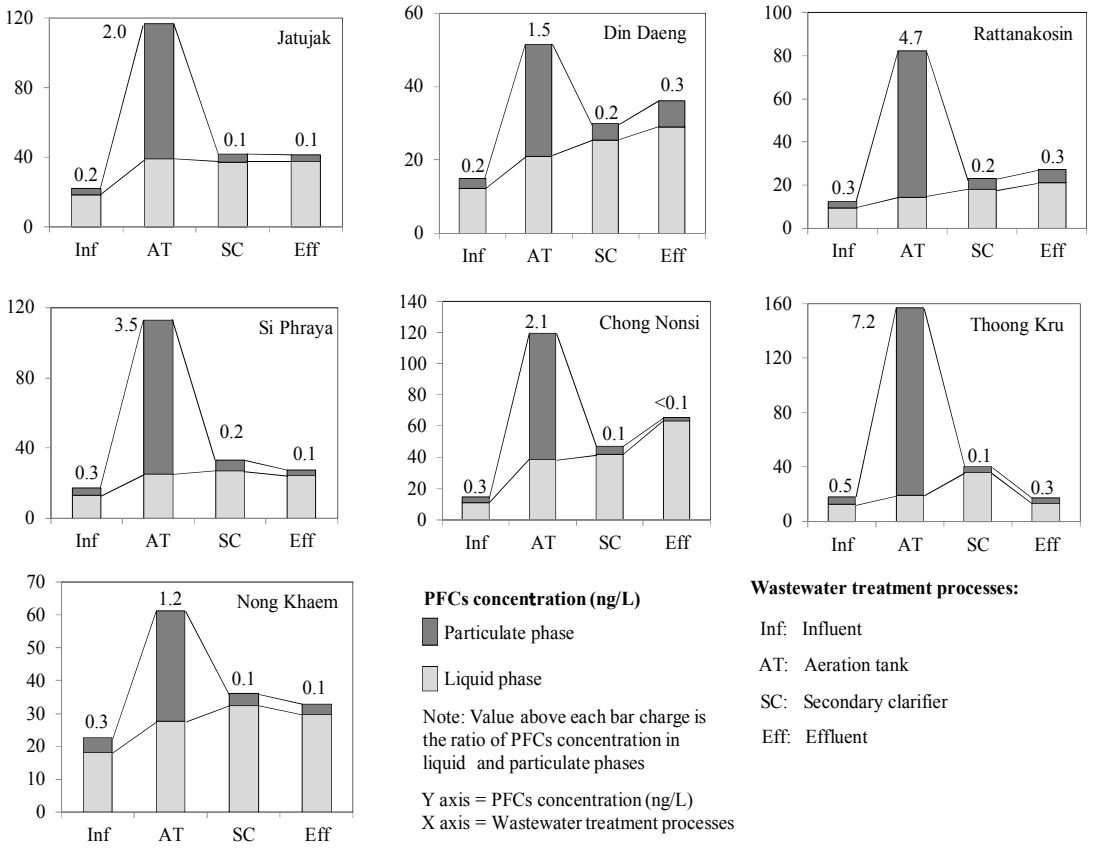


Figure 3.4 Comparison of total PFCs concentration (ng/L) in each municipal wastewater treatment processes both liquid and particulate phases

In liquid and particulate phases, the PFCs concentrations in influents are almost similar in all MWWTPs, which had lower PFCs concentration than aeration, secondary clarifier, and final effluent. As wastewater reaches into aeration process, the concentrations of

PFCs increased by many folds than compared with influent samples. Particularly, its concentration in the particulate phase samples increased 2 to 7 times higher than in the liquid phase. An increase of PFCs concentration in aeration process is a common phenomenon in WWTPs as many researchers have reported (Yu *et al*., 2009; Loganathan *et al*., 2007). PFCs concentration can be increased by two main reasons.

1. Probably due to transformation of precursors into PFCs at aeration process and it is a widely discussed possibility among the researchers (Boulanger *et al*., 2005; Bossi *et al*., 2008; Wang *et al*., 2005; Martin *et al*., 2005). Biotransformation of precursors such as *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE) and *N*-ethyl perfluorooctane sulfonamido acetic acid (*N*-EtFOSAA) into PFOS and fluorotelomer alcohols into PFCAs were often mentioned in those studies.

2. Another reason could be the adsorption/bioaccumulation of PFCs from fresh batch of wastewater into activated sludge. Each batch of wastewater is retained in the aeration tank for a certain period of time (hydraulic retention time, HRT), which mixes with activated sludge which, in addition, is retained in the aeration tank for several days (sludge retention time, SRT) and also recirculated. Hence, repeated contact of activated sludge with fresh batch of wastewater containing PFCs for several days, increases concentration of PFCs adsorption/bioaccumulation into activated sludge. Furthermore, the hydrophobic properties of PFCs also enhance their adsorption into activated sludge (Zhou *et al*., 2010).

In the secondary clarifier, PFCs concentration in the particulate phase decreased than from aeration process because of sludge separation. However, PFCs concentration in liquid phase increase that could be due to degradation of PFCs precursors, desorption of PFCs from particulate phase, or matrix interference in the samples. All MWWTPs investigated in this study found higher PFCs concentration in effluent than in the influent. In effluent, most of MWWTPs showed similar or an increase of PFCs concentration in the liquid phase, since all MWWTPs used activated sludge, which was

returned from the secondary clarifier. PFCs level in the particulate phase increased in the aeration tank and it could be from the sludge system. Therefore, it shows that PFCs are not removed effectively by activated sludge process.

3.5.3 Behavior of PFCs in liquid and particulate phases

Activated sludge is a conventional treatment process and it has been reported that it is not sufficient to remove PFCs. High concentrations of PFCs were detected in the aeration tank in both liquid and particulate phases. Therefore, PFCs behavior in aeration was observed. The percentage of each PFC in both liquid and particulate phases from all MWWTPs was shown in **Fig. 3.5**. The graph shows the percentage of each PFC adsorbed on particulate phase. In PFASs group, it was found that PFOS (>99%) was more adsorbed on particulate phase than PFHxS (62%) and PFBuS (1%). The adsorption potential of PFCs increased with increasing number of carbon chains. PFCAs also showed similar trend and long carbon-chain were more adsorbed on activated sludge than shorter carbon-chain ones. Particularly, PFUnDA and PFDoDA were long carbon-chain PFCs which were non-detectable in most effluent samples. It could be explained that those compounds were highly adsorbed on the particulate phase at 72% and 89%, respectively.

Longer carbon-chain PFCs were more hydrophobic than shorter ones. Therefore, hydrophobic interaction was an important mechanism of PFCs adsorption on activated sludge. Moreover, perfluorinated surfactants were reported to be more hydrophobic than hydrocarbon ones (Tanford, 1980). Several studies reported that organic carbons in sediment were a dominant parameter affecting PFCs adsorption, indicating the importance of hydrophobic interaction (Higgins and Luthy, 2006; Pan *et al*., 2009). At an equal_perfluorocarbon chain, it was found that the sulfonate was more adsorbed on particular phases than carboxylate due to stronger hydrophobicity. For example, PFOS and PFNA have the same length of perfluorocarbon chain and also PFHxS and PFHpA. PFOS (> 99%) was adsorbed more in the particulate phase than PFNA (8%) and PFHxS (62%) was also adsorbed more than PFHpA (29%), respectively. Zhou *et al*. (2010) reported that PFOS was highly adsorbed on activated sludge higher than PFBuS,

PFHxA, PFHxS, PFOA and PFDoDA. Overall, the higher PFCs concentration was detected in the particulate phase in activated sludge process. Therefore, return sludge could cause the increasing of PFCs concentration due to their accumulation during the process.

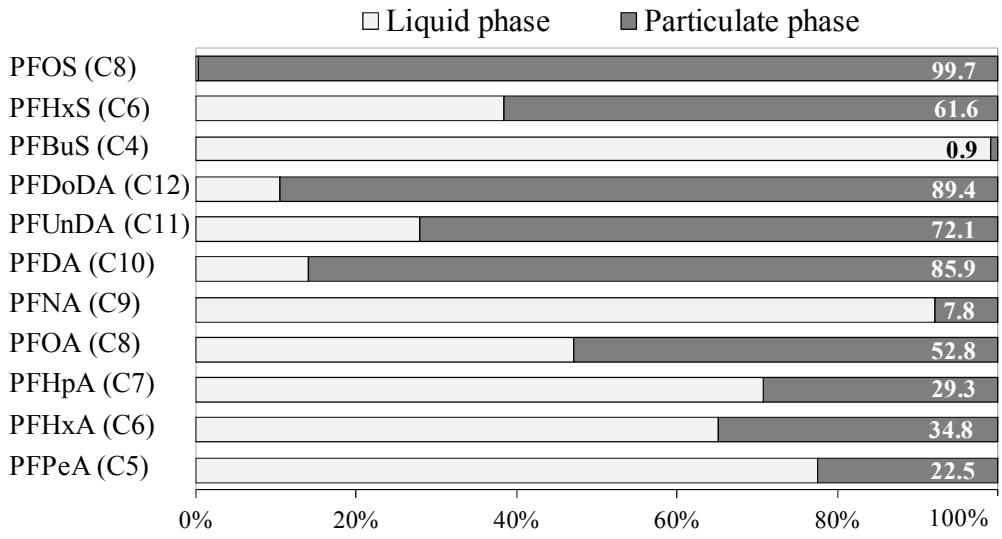


Figure 3.5 PFCs distribution in liquid and particulate phases in the aeration tank

3.5.4 Comparison with other countries

Several countries have reported an increase in level of PFCs concentration in effluent from MWWTPs. In this study, PFOS and PFOA were found in higher concentration than other types of PFCs. Similarly, high concentrations of PFOS and PFOA were detected in MWWTPs in several countries. **Figure 3.6** shows the comparison of PFOS and PFOA concentrations in effluents among various countries (Germany (Ahrens *et al*., 2009), Denmark (Bossi *et al*., 2008), Korea (Guo *et al*., 2010), Taiwan (Lin *et al*., 2010), Hong Kong (Ma and Shih, 2010) and Singapore (Yu *et al.*, 2009). It showed that PFOS was found in lower concentration than other countries, except Germany and Korea, while PFOA was found in lower concentration than in other countries except Hong Kong. The concentrations of both PFOS and PFOA in this study were less than 10 ng/L, which is comparatively lower than other countries.

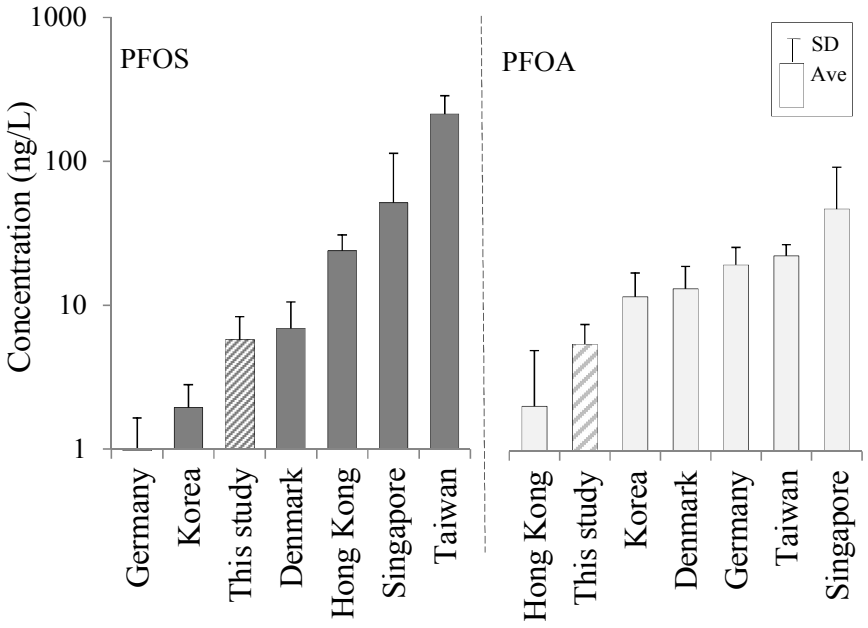


Figure 3.6 Comparing PFOS and PFOA concentrations in effluent of MWWTPs with other countries

The reason could be sewerage system in Bangkok which has the combined sewer system where the wastewater discharged from the household had mixed with storm water (BMA, 2001). Therefore, it had the dilution effects on the PFOS and PFOA concentrations. Moreover, the survey was conducted during rainy season so there is high possibility of rain water dilution. Thus, the repetition of sampling should be done in the dry season for further studies.

3.5.5 PFCs contamination in industrial wastewater

The industrial wastewater is the major source of PFCs discharged into water environment. In Thailand, there are many industries which are located in particular area called industrial estate (IE). All industries discharge wastewater into central WWTP in IE. In this study, five IWWTPs which have not been reported PFCs concentration were selected. Tap water, influent and effluent of each IWWTP was collected to examine the

removal of PFCs in wastewater treatment process. Tap water samples were collected to identify the background of PFCs level entering into the industries. All PFCs were detected in most samples above *LOQ* except for PFUnDA and PFDoDA. The total PFCs concentration in tap water was ranged from 3.2 to 7.5 ng/L. This tap water is used for the workers of IEs for their daily life activities and for the industrial processes.

Table 3.7 shows the PFCs concentration in tap water were much lower than in wastewater. It means PFCs were applied in the production processes and discharged along with the wastewater. Wastewater from each industry inside the industrial estate was discharged to the central WWTP facility. Different types of wastewater from various industries were mixed in the equalization tank before moving to biological processes. All IWWTPs used activated sludge treatment process. Only IE5, treated wastewater was passed through sand and GAC filtration before discharging. Influent samples were collected after the equalization tank in each industrial estate.

Table 3.7 Concentrations of PFCs (ng/L) in tap water influent and effluent from IWWTPs

PFCs	IE1				IE2				IE3				IE4				IE5			
	Inf	Eff	Eff/Inf	Tap	Inf	Eff	Eff/Inf	Tap	Inf	Eff	Eff/Inf	Tap	Inf	Eff	Eff/Inf	Tap	Inf	Eff	Eff/Inf	Tap
PFBuS	39.5	48.9	1.2	ND	11.7	23.2	2.0	ND	3.2	20.0	6.3	ND	71.1	78.1	1.1	ND	203.0	156.3	0.8	ND
PFHxS	<LOQ	ND	-	ND	0.9	3.2	3.6	ND	6.6	16.0	2.4	ND	0.9	8.5	9.1	0.9	37.7	37.4	1.0	1.9
PFOS	15.2	33.0	2.2	0.3	8.2	11.5	1.4	0.5	ND	6.3	6.3	0.7	1.8	8.2	4.6	0.6	315.5	373.5	1.2	0.8
PFPeA	12.9	15.4	1.2	ND	0.9	1.4	1.6	ND	1.3	4.0	3.1	2.2	1.7	31.8	18.4	1.7	<LOQ	10.0	10.0	0.2
PFHxA	5.9	13.0	2.2	0.7	2.2	4.7	2.1	1.4	0.8	2.5	3.2	1.7	3.6	10.9	3.0	1.1	5.1	16.7	3.3	0.3
PFHpA	2.9	11.3	3.9	0.1	1.2	6.3	5.1	0.3	1.6	2.9	1.8	0.4	2.2	18.8	8.4	0.2	5.1	35.6	7.0	0.3
PFOA	19.2	36.5	1.9	0.3	4.8	19.3	4.0	0.6	2.2	6.6	3.0	1.5	4.5	40.8	9.1	0.5	15.0	8.9	0.6	0.7
PFNA	4.5	11.5	2.5	<LOQ	ND	2.2	2.2	0.9	1.5	3.4	2.2	1.0	ND	ND	ND	ND	15.6	22.4	1.4	0.8
PFDA	2.2	3.1	1.4	1.8	2.3	5.8	2.5	3.6	ND	1.1	1.1	<LOQ	2.2	14.6	6.7	2.2	<LOQ	<LOQ	-	0.1
PFUnDA	ND	ND	-	ND	<LOQ	<LOQ	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-	ND
PFDoDA	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-	0.2
∑PFCs	102.3	172.7	16.6	3.2	32.3	77.6	24.5	7.3	17.1	62.7	29.6	7.5	88.0	211.6	60.3	7.3	596.8	660.6	25.3	5.2

Total PFCs concentration in effluent ranged from 62.7 to 660.6 ng/L, which was much higher than in MWWTPs because PFCs were used in a variety of industrial processes. All IEs were found that PFCs concentration in effluent were higher than influent which were similar to MWWTPs. The activated sludge treatment technique was ineffective to remove PFCs, which led to increase the concentration of PFCs in effluent. The highest

concentration of PFCs in the effluent was found in IE5 followed by IE4, IE1, IE2, and IE3, respectively as shown in **Fig. 3.7**.

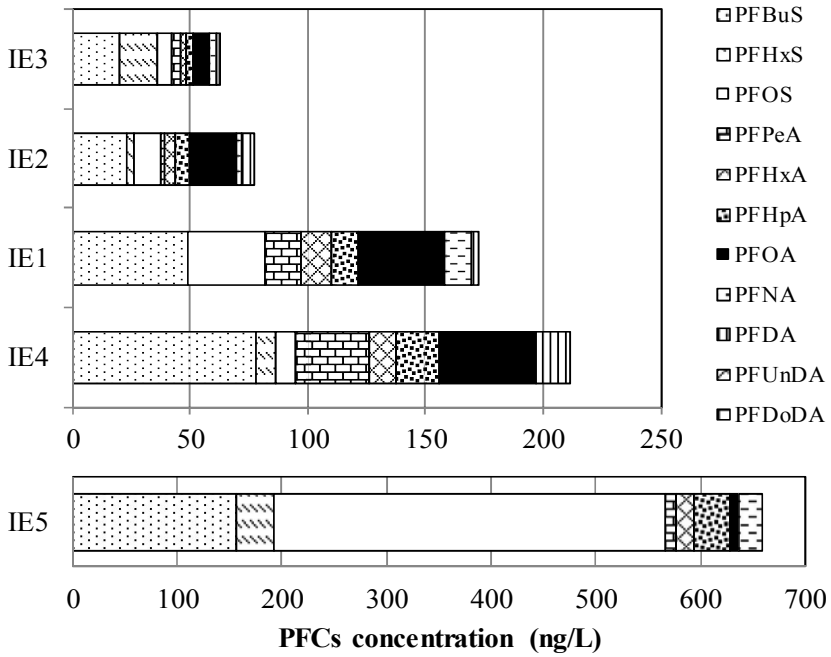


Figure 3.7 Percentage of PFCs in effluent of each IWWTP

Among 11 PFCs, PFBuS was the dominant PFCs which showed high concentration in most of effluent of IEs. In 2008, the different IEs in Thailand were investigated PFCs concentration in final effluent (Shivakoti *et al*., 2010). They also detected high concentration of PFBuS in one effluent of IE. This result could indicate that some industries might be adopting PFBuS due to widespread concern on the uses of PFOS.

The elevated PFCs concentration in effluent were detected at IE5 (660.6 ng/L) and the dominant PFCs were PFBuS and PFOS which were 156.3 and 373.5 ng/L, respectively. Most of PFCs were detected except two long-carbon chains of PFCs, which were PFUnDA and PFDoDA. In PFASs group found that PFBuS was found higher concentration than PFHxS and PFOS except IE5. High concentration of PFBuS was detected due to substitution of PFOS as mentioned earlier in MWWTPs. In PFCAs group, high PFOA concentration was detected in most of IWWTPs. At IE5, several

automotive industries are located in IE5. Those industries often use PFOS in the production processes, thus high PFOS concentration was found in effluent. In addition, European commission (2011) reported PFOS has been used in the automotive industry. Though, IE5 has sand filtration and GAC filtration processes. However, PFCs was still detected at high concentration in effluent. Therefore, sand filtration and GAC filtration were not sufficient to remove PFCs. In addition, water purification plants with advanced treatment processes have been found that PFCs were not removed effectively by GAC filtration (Shivakoti *et al*., 2010).

Figure 3.8 shows the comparison of PFOS and PFOA concentrations with other countries. The concentrations of PFOS and PFOA in industrial wastewater depend on the manufacture productions. In Thailand, the PFOS concentration in this study was higher than previous survey (Kunacheva, 2009) and the maximum concentration is as high as in Austria and Singapore. New York had the lowest concentration of PFOS in effluent of industrial wastewater.

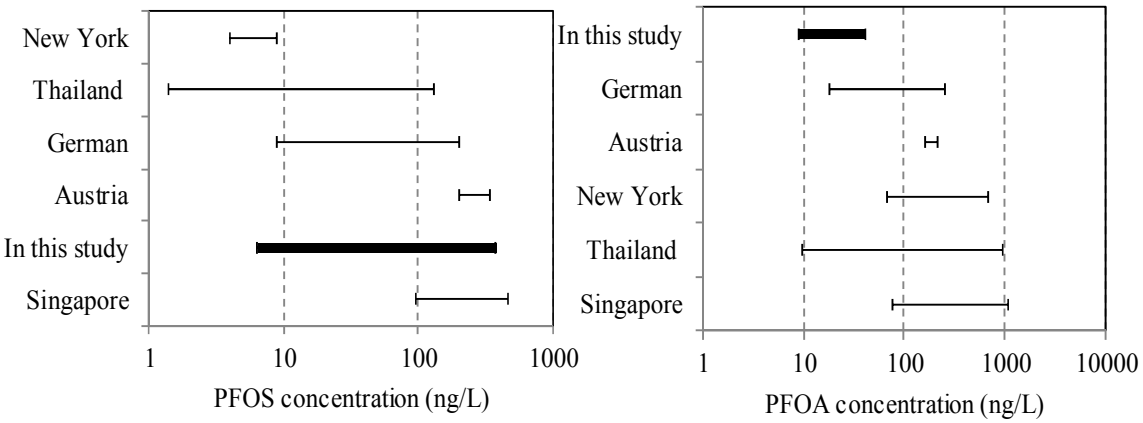


Figure 3.8 Comparing PFOS and PFOA concentrations in effluent of IWWTPs with other countries (Sinclair *et al*., 2006; Kunacheva, 2009; Becker *et al*., 2009; Clara *et al*., 2008; Yu *et al*., 2009)

In this study, the lowest range of PFOA concentration was detected in effluent of industrial wastewater. Since, varieties of industries were located in industrial estates in Thailand, PFOS and PFOA were found in wide range than compared to other countries.

Dilution of PFOS and PFOA concentration in Thai industrial wastewater occurred due to combined wastewater system from all industries. However, high concentration of PFOS and PFOA can be expected at discharge point of each industry

3.6 Summary

PFCs concentration was investigated in seven municipal and five industrial WWTPs in Thailand. MWWTPs were sampled at influent, aeration tank, secondary clarifier and effluent. Influent and effluent were collected from central WWTPs of five industrial estates. Tap water was also collected to identify the background concentration of the industrial estates.

1. Among seven MWWTPs, Chong Nonsi had the highest concentration of PFCs in effluent at 63.6 ng/L. The major PFCs contaminations in the effluent were PFOS and PFOA.
2. Biological processes were not effective to remove PFCs. The total PFCs in effluent increased approximately by 2.5 times than compared with influent.
3. In comparison to other countries, lower level of PFOS and PFOA (less than 10 ng/L) were observed in Bangkok MWWTPs. Due to the combined sewerage system in Bangkok, the wastewater discharged from the household is mixed with storm water, which affected PFOS and PFOA concentrations.
4. IE5 had the highest concentration of PFCs at 660.6 ng/L in effluent. The major PFCs in the effluent were PFBuS (156.3 ng/L) and PFOS (373.5 ng/L). The high concentration level of PFBuS was detected in all IWWTPs due to substitution of PFOS.
5. Industrial wastewater was the major source of PFCs released into the environment. So, effective removal techniques should be applied to minimize environmental impact, which was explained in next chapter.

Chapter 4

Adsorption of PFCs by batch experiments

4.1 Introduction

As the conventional treatment techniques are not sufficient to treat PFOS and PFOA so it is necessary to develop the alternative treatment methods and technological innovations. Conventional adsorbents such as activated carbon are being used by some PFCs' manufacturers to remove PFCs from their industrial wastewater. The adsorption capacities of activated carbon are not high enough to reduce the concentration of PFCs in the wastewater to acceptable level (Ochoa-Herrera and Sierra-Alvarez, 2008; Yu *et al*., 2009), hence the resultant PFCs in the discharge cause contamination to the water bodies. Anion exchange resin could be one of the potential techniques to remove PFOS and PFOA from aqueous solutions as these compounds present in anionic form in solution. To date, only a few researchers have studied efficiencies pertaining to anion exchange resins to remove PFOS and PFOA in water (Deng *et al*., 2010; Senevirathna *et al*., 2010; Yu *et al*., 2009). Furthermore, the adsorption behaviors of resins are poorly understood as the resins possess variety of properties that influenced their adsorption efficiencies.

Kinetic experimental data reveals adsorption velocity and thus are important for the design and operation of processes. It is widely accepted that adsorption process contains four major steps from liquid phase to sites on porous surface as (1) diffusion in liquid phase, (2) external mass transfer to particle surface, (3) internal diffusion inside of adsorbent including (a) porous diffusion and (b) surface diffusion and (4) attachment onto the sites (Weber and Smith, 1987).

An adsorption isotherm describes the equilibrium of the sorption of a material on a surface (more general at a surface boundary) at a constant temperature. It represents the

amount of material bound at the surface (the sorbate) as a function of the material present in the solution. The adsorption isotherms are very often used as empirical models to estimate adsorption capacities (Atkin, 1998). *Freundlich* and *Langmuir* equations are widely applied for water and wastewater treatment processes among the number of isotherm equations suggested with some assumptions. *Freundlich* equation is the only possible isotherm equation to model the experimental data at low equilibrium concentrations.

Freundlich equation is an empirical relationship which describes the adsorption of solutes from a liquid surface to a solid surface. It is widely applied to describe the adsorption process for many compounds onto heterogeneous surfaces, including activated carbon, metals and polymers in diluted solutions (Robert *et al*., 2000; Sirinivasan *et al*., 2008). The *Freundlich* equation (Freundlich, 1906) is shown in **Eq. (4.1)**.

$$q_e = K_f C_e^{1/n} \tag{4.1}$$

Where K_f(mg/g)/(mg/L)$^{1/n}$ is *Freundlich* adsorption constant or capacity factor, and n is *Freundlich* exponent which provides a measure for adsorption intensity. If n = 1, partition between two phases is independent of concentration and isotherm become linear. q_e (mg/g) is a concentration of adsorbate on adsorbent, while C_e (mg/L) is an equilibrium concentration of the adsorbate.

The *Freundlich* isotherm is known to be operative only within certain concentration limits. This is because, given an exponential distribution of binding sites, the number of sites increases indefinitely with a decreasing association constant, implying that there are an infinite number of sites. However, the *Freundlich* isotherm will be a more accurate approximation at lower concentrations (Robert *et al*., 2001). Most of the adsorbents tested in this study are widely used in water and wastewater treatment, particularly for organics. The adsorptive capacities of tested polymers at low concentrations were calculated with the *Freundlich* constant determined by the experiment.

4.2 Objectives

The main objective of this study was to examine effectiveness of five commercial anion exchange resins and GAC on removal of PFCs. To achieve the main objective, four specific objectives were established as follows:

1. To examine the PFOS and PFOA adsorption kinetics of five anion exchange resins and GAC
2. To examine the PFOS and PFOA adsorption capacities of anion exchange resins and GAC
3. To investigate the adsorption of single PFCs and mixed PFCs onto selected adsorbents
4. To investigate the effects of temperature, pH and ionic strength on adsorption on PFCs onto selected adsorbents

4.3. Methodology

4.3.1 Selection of anion exchange resins

There are various kinds of resins, which have different properties such as polymer matrix, functional group, ion exchange capacity, diameter, swelling percentage, moisture retention capacity. PFCs are present as anion in aqueous solution, so anion exchange becomes a suitable technique for their removal. Five anion exchange resins were selected because they are widely used in water/wastewater treatment. All resins used in this study were gel type, which has hydrophilic properties. Since, hydrophilic polymers can enhance diffusion of PFCs onto ion exchange sites. In addition, to understand the effect of functional group, PFA300 (type II) was selected. PFA400 and PFA444 were used because they were almost similar as PFA300 but their functional groups were type I. IRA400 has been reported to have high adsorption capacity for both PFOS and PFOA at high equilibrium concentration of 1 mg/L (Yu *et al*., 2009). Thus, IRA400 was selected to test with lower equilibrium concentration in this study. In addition, Dow Marathon A and IRA400 were from different company which have different properties to others. The effects of resin properties were explained in Section 4.4.3.

4.3.2 Anion exchange resins preparation

Five kinds of anion exchange resins were utilized in this study. Three anion exchange resins were obtained from Purolite Company coded as PFA300, PFA400, PFA444 and two other anion exchange resins were Dow Marathon A (Dow Chemical) and Amb IRA400 (Sigma Aldrich). Adsorbents were washed with ultrapure water several times and methanol (LC/MS grade) to remove dirt and avoid contamination of PFCs. They were then again washed with ultrapure water to remove residual methanol and dried at 50ºC to obtain constant weight (approximately 2 days). Ion exchange resins are insoluble material which have diameter in range of 0.5 – 1 mm. Most of commercial resins are made of polystyrene and copolymerized by divinylbenzene. Strong base anion exchange resins were classified as type I and type II based on their functional groups. Anion exchange resins containing strong basic trimethylbenzylammonium group were classified as type I, and those containing dimethylethanolaminium group were classified as type II. The characteristics of each resin are shown in **Table 4.1**.

Table 4.1 Characteristics of anion exchange resins used in this study

Adsorbents	Matrix	Functional group[d]	Diameter (mm)	Ion exchange capacity (eq/L)	Swelling (%)	Moisture retention capacity (%)
PFA300[a]	Polystyrene cross-linked DVB	$R\text{-}(CH_3)_2(C_2H_4OH)N^+$ (Type II)	0.56	1.4	10	43
PFA400[a]	Polystyrene cross-linked DVB	$R\text{-}(CH_3)_3N^+$ (Type I)	0.57	1.3	20	53
PFA444[a]	Polystyrene cross-linked DVB	$R\text{-}(CH_3)_3N^+$ (Type I)	0.57	1.1	25	58
Dow Marathon A[b]	Styrene-DVB	$R\text{-}(CH_3)_3N^+$ (Type I)	0.58	1.3	20	55
Amb IRA400[c]	Styrene-DVB	$R\text{-}(CH_3)_3N^+$ (Type I)	0.60 – 0.75	1.4	NA	NA

Note: All resins are gel type. DVB is divinylbenzene. NA is not available.

a. Purolite company (www.purolite.com)
b. Dow chemical company (www.dowex.com)
c. Sigma-Aldrich company (www.sigmmaldrich.com)
d. Functional group of resin type I is trimethylbenzylammonium and type II is dimethylethanolaminium

4.3.3 GAC preparation

Coal-based activated carbon of Filtrasorb 400 was purchased from Calgon Mitsubishi Chemical. Firstly, GAC was transferred into boiled ultrapure water for one hour to remove preloaded organics and fine particles. Floating impurities and grease were removed from surface of boiling water. Soon after boiling, GAC was flushed with abundant ultrapure water to cool it down and clean the carbon. After intensive washing, it was in ultrapure water and stored at room temperature overnight to equilibrate surface properties. The water was discarded and GAC was moved into an oven and dried at 105°C for two days to remove moisture inside pores completely. Dried GAC was stored in polypropylene (PP) bottles with airtight covers to prevent exposure to atmosphere and possible adsorption of moisture and organics from air.

In order to obtain GAC in required diameters, the dried GAC was pulverized using a mortar and pestle. Then the crushed GAC was separated by sieving in required ranges of diameters (0.25-0.50 mm). The fine particles or powders attached on the surface of crushed GAC during pulverization should be removed before experiments. Therefore, sieved GAC was washed again with ultrapure water, and the supernatant with fine particles of carbon were decanted carefully. The cleansing process was repeated several times until the water over GAC granules was clean and clear. GAC was again dried in oven at 105°C for two days and stored in airtight bottles. Benefiting from former cleaning process, granular materials can be precisely weighed before experiments.

After weighing, dried granular materials were moved into PP valves and soaked in small amount of ultrapure water to pre-wet inner pores and applied in a vacuum for 24 hours. This step was important and necessary because air inside pores might adversely reduce adsorption capacity and velocity (Nicholas and Paul, 1993). After pre-wetting, excessive water was discarded by pipette and the materials were added to the bottles filled with PFCs solutions. The total pore volume of GAC is 0.61 cm^3/g. Amount of macropores (>500 Å) mesopores (20-500 Å) and micropores (<20 Å) are 0.04, 0.09 and 0.48 cm^3/g, respectively. Surface area is 900 – 1100 cm^2/g.

4.3.4 Adsorption kinetics

PFCs were prepared in 100% acetonitrile (LC/MS grade) and stored in polypropylene (PP) bottle at 4°C. The stock solutions of PFCs were diluted at different concentrations using 40% acetonitrile of ultrapure water purified with 18.2 MΩ *Milli-Q* (Millipore SAS 67120) water purification systems. PFCs solutions in 40% acetonitrile in ultrapure water were used in batch experiments.

Batch experiments were conducted to study the adsorption kinetics of PFOS and PFOA onto the five anion exchange resins (PFA300, PFA400, PFA444, Dow Marathon A and IRA400) and GAC by using a bottle-point technique. Adsorbent (10 mg) was placed into 125 mL PP bottles. Then, 100 mL each of PFOS and PFOA with concentration of 0.5 mg/L were added into PP bottles. The kinetic experiments were carried out by Thermo shaker (EYELA-NTS4000) (at 120 rpm and 25ºC). Samples were collected at different contact times of 1, 3, 6, 12, 24, 48, 72 and 96 hours. Control bottles without adsorbents were run in parallel to check for possible removal of PFOS and PFOA by other mechanisms than adsorption. All experiments were replicated 3 times (n = 3) and the average value was adopted for reporting.

4.3.5 Adsorption isotherms

Adsorption isotherm experiments were carried out with similar adsorbents as in kinetic studies. Adsorbent (1 mg) was placed into 125 mL PP bottles that contained single solute of PFC or mixed PFCs 100 mL at varying initial concentrations of 0.01 – 1.00 mg/L. There were three samples for each concentration with a replication (n = 3). Thermo shaker (EYELA-NTS4000) was set at 120 rpm, 25ºC and shaken for 96 hours. A control without adsorbents was added to each concentration of PFCs. After shaking, adsorbent was immediately separated from the sample and sample was diluted into 40% acetonitrile in ultrapure water. The samples were analyzed by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). The summaries of experimental conditions are shown in **Table 4.2**.

4.3.6 Effects of temperature, pH and ionic strength

Effects of temperature on adsorption of PFOS and PFOA onto PFA300 was studied. The temperature was studied at 10, 20, 30, 35, 40, 45 and 50°C. Adsorbent (5 mg) was placed into 125 mL PP bottles that contained PFOS or PFOA (1 mg/L) 100 mL and shaken at 120 rpm for 48 hours in a thermostatically controlled shaker at a pre-set temperature.

Table 4.2 Summary of experimental conditions for kinetics and isotherms

Experiments	Target PFCs	PFCs conc. (mg/L)	Adsorbents	Amount of adsorbent (mg)	Contact time (h)
Kinetic	PFOS & PFOA	0.5	PFA300, PFA400, PFA444, IRA400 Dow Marathon A, & GAC	10	1, 3, 6, 12, 24, 48, 72 & 96
Isotherm	PFOS & PFOA	0.01, 0.05, 0.1, 0.5 & 1.0	PFA300, PFA400, PFA444, IRA400 Dow Marathon A, & GAC	1	96
Isotherm of single PFC	PFBuS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA & PFOA	0.01, 0.05, 0.1, 0.5 & 1.0	PFA300	1	96
Isotherm of mixed PFCs	PFBuS, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA & PFDoDA	0.01, 0.05, 0.1, 0.5 & 1.0	PFA300	1	96

Batch experiments were conducted to study effects of pH on adsorption of PFOS and PFOA onto PFA300. pH was studied at 3, 5, 7, 9 and 11 which were adjusted by adding negligible volume of 0.1 M NaOH and 0.1 M HCl. Initial PFOS or PFOA concentration was 1 mg/L. Thermo shaker was set at 120 rpm, 25ºC and shaken for 48 hours.

Another series of batch experiments were carried out to study the effects of ionic strength on adsorption of PFOA onto PFA300. NaCl was used in this study which was prepared at 0.1, 1, 10, 100, and 1000 mM and the PFOA concentration was 1 mg/L. The experimental condition on the effects of temperature, pH and ionic strength are shown in **Table 4.3**.

Table 4.3 Summary of experimental conditions for temperature, pH and ionic strength studies

Experiments	Value	Target PFCs	PFCs conc. (mg/L)	Adsorbent	Amount of adsorbent (mg)	Contact time (hours)
Temperature (°C)	10, 20, 30, 35, 40, 45 & 50	PFOS & PFOA	1	PFA300	5	48
pH	3, 5, 7, 9 & 11	PFOS & PFOA	1	PFA300	5	48
Ionic strenght	1, 10, 100, & 1000 mM	PFOA	1	PFA300	5	48

The amount of PFOS and PFOA adsorbed onto PFA300 in temperature, pH and ionic strength experiments were calculated as shown in **Eq. (4.2)**.

$$q_e = \frac{(Initial\ conc.(mg/L) - Equilibrium\ conc.(mg/L))}{Amount\ of\ adsorbent\ (g)}\ x\ sample\ volume\ (L) \qquad (4.2)$$

Calibration curve and quantification

The calibration curve used for quantification consisted of five concentrations of PFCs standard which were 0.1, 0.5, 1.0, 5.0 and 10.0 µg/L and linearity with determination coefficients (R^2) was more than 0.99. Therefore, for all experiments the analytes can be reliably quantified by the instrument. **Table 4.4** shows instrument detection limit (*IDL*) and instrument quantification limit (*IQL*).

Table 4.4 *IDL* and *IQL* of PFCs for laboratory experiments

	PFBuS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
IDL (µg/L)	0.02	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.02	0.01	0.01	0.01
IQL (µg/L)	0.08	0.04	0.04	0.05	0.06	0.07	0.04	0.03	0.06	0.02	0.03	0.05

4.4 Results and discussion

4.4.1 Kinetic study

Adsorption kinetic describes the absorption rate of PFOS and PFOA of resins over time. The equilibrium state was established more rapidly in PFA300 followed by Dow Marathon A, PFA400, PFA444 and IRA400, respectively for both PFOS and PFOA as shown in **Fig. 4.1**. All resins showed a faster absorption rate of PFOS than PFOA. The kinetic patterns of these two compounds were almost similar. However, it was observed that PFOS was slightly faster adsorbed than PFOA due to the more hydrophobic properties of PFOS. PFOS was adsorbed at one hour of shaking time while the concentration of PFOA was still remained as in initial concentration.

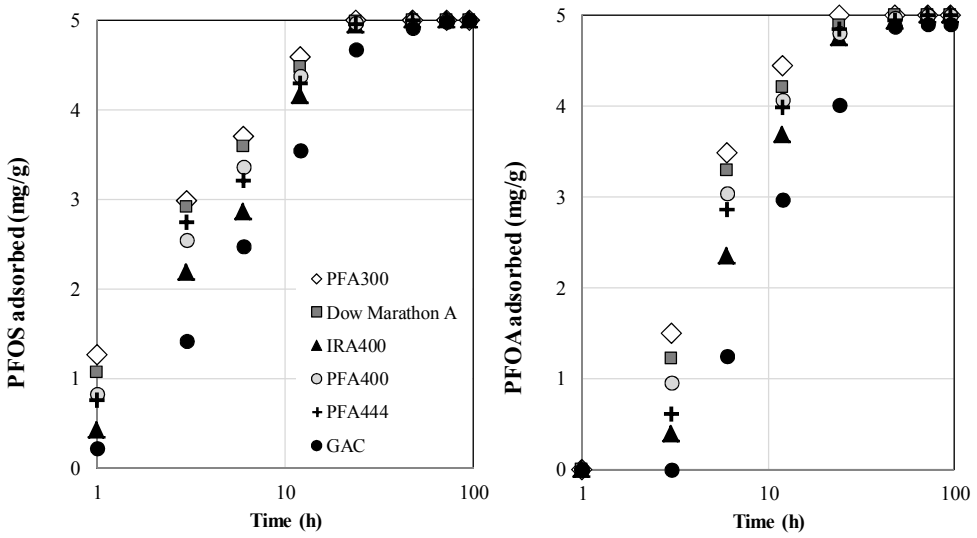


Figure 4.1 Kinetic studies of five anion exchange resins and GAC on adsorption of PFOS and PFOA

PFA300 showed the fastest adsorption for both PFOS and PFOA because PFA300 contained one -OH group in functional group which not only affected adsorption capacity (discussed in section 4.4.2) but also adsorption rate. Having -OH group can make PFA300 more hydrophilic and possess a more open structure compared to other

resins (Bolto *et al*., 2002; Deng *et al*., 2010), and results in faster diffusion of PFOS and PFOA molecules into the anion exchange sites.

IRA400 was found to have low adsorption rate when compared with other resins used in this study. That is probably due to low intra-particle diffusion of PFOS and PFOA onto IRA400. Several researchers have found that adsorption process of main solutes into ion exchange resins in a well-mixed solution was dominated by intra-particle diffusion (Zhao and Sengupta, 2000). Furthermore, IRA400 had the largest sized resin beads, effecting adsorption rate of PFOS and PFOA. Yu *et al*. (2009) found that adsorbate easily diffuses into powdered activated carbon (PAC) at a faster rate than GAC due to smaller particle size. In case of Dow Marathon A, PFA400 and PFA444, adsorption rate were different due to their ion exchange capacity.

From the kinetic results, it can be concluded that adsorption rate of PFOS and PFOA onto resins were affected by chemical properties (PFOS and PFOA), functional group of resin, ion exchange capacity and size of resin bead, respectively. Deng *et al*. (2010) found that IRA400 required more time to reach adsorption equilibrium on adsorption of PFOS. Moreover, GAC had high proportion of micropores which took longer for PFOS and PFOA to enter into their pores; hence it took the longest time to reach the equilibrium state.

4.4.2 Adsorption isotherms of PFOS and PFOA onto anion exchange resins

Five commercial anion exchange resins were selected for this study which was generally used for water and wastewater treatment. Anion exchange resins were different in terms of functional groups, ion exchange capacities and bead size (Table 4.1).

Figure 4.2 shows the adsorption amounts of PFOS and PFOA onto adsorbents at different equilibrium concentrations. The shaking duration of the isotherm experiment was 96 hours to ensure that all adsorbents reached their equilibrium concentrations.

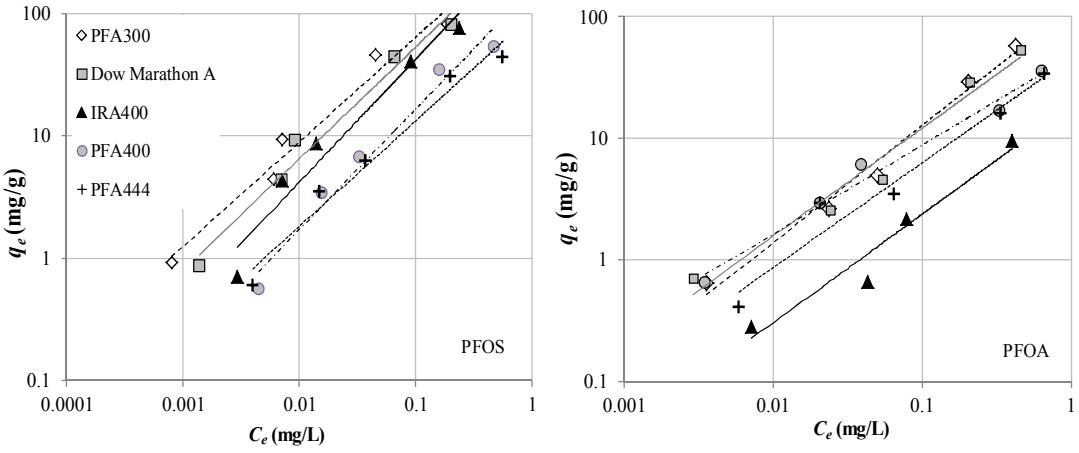


Figure 4.2 Adsorption isotherms of PFOS and PFOA onto the five anion exchange resins by using *Freundlich* model.

Table 4.5 *Freundlich* isotherm constants for the adsorption of PFOS and PFOA onto anion exchange resins and GAC

PFCs	Adsorbent	K_f (mg/g)/(mg/L)$^{1/n}$	$1/n$	R^2
PFOS	PFA300	455.2	0.85	0.97
	Dow Marathon A	431.6	0.91	0.98
	IRA400	425.5	1.00	0.95
	PFA400	158.6	0.98	0.97
	PFA444	96.6	0.86	0.97
	GAC	163.0	0.82	0.98
PFOA	PFA300	117.4	0.96	0.99
	Dow Marathon A	93.0	0.89	0.97
	IRA400	18.4	0.90	0.94
	PFA400	47.3	0.73	0.98
	PFA444	45.7	0.86	0.96
	GAC	39.9	0.73	0.97

Note: IRA400 adsorbed PFOA up to 0.5 mg/L.

Adsorption capacity of anion exchange resins with different concentrations (in the range of 0.01 – 1.00 mg/L) of PFOS and PFOA were determined by fitting with the *Freundlich* model. The *Fruendlich* isotherm is used to describe the adsorption of

solutes from liquid to a solid surface. It is also widely used to describe the adsorption process on heterogeneous surfaces of many compounds (Robert *et al.,* 2001). All of the adsorbents fitted well with *Freundlich* isotherm (PFOS, R^2 = 0.95 – 0.98; PFOA, R^2 = 0.92 – 0.99). *Freundlich* adsorption constants determined for tested adsorbents are listed in **Table 4.5**.

The adsorption capacities of PFOS were in the range of 97 – 455 mg/g while those of PFOA were in the range of 18 – 117 mg/g. It was found that all of the adsorbents can adsorb PFOS better than PFOA which can be explained by their chemical properties. Substitution of functional group on PFOS and PFOA were different as sulfonates and carboxylates, respectively. Higgins and Luthy (2006) found that sulfonates had stronger adsorption onto sediments when compared to carboxylates with equal carbon chain length, so that could be one reason for higher adsorption of PFOS on resins than PFOA. Moreover, hydrophobic interaction can occur in this experiment. Zhou *et al*. (2010) reported that PFOS have shown more hydrophobic properties than PFOA. Higgins and Luthy (2006) also reported higher adsorption of PFOS than PFOA on the sediment because of hydrophobic interaction in the adsorption process.

The adsorption capacities of PFOS onto resins in order of K_f (*Freundlich* adsorption capacity) were found to be, PFA300 > Dow Marathon A > IRA400 > PFA400 > PFA444; while for PFOA they were in order of PFA300 > Dow Marathon A > PFA400 > PFA444 >IRA400. The fitting of *Freundlich* model displayed high linearity according to values of $1/n$ close to one (0.85 – 1.00 for PFOS and 0.73 – 0.96 for PFOA) indicating that hydrophobic partition probably occurs in adsorption. Deng *et al.* (2010) found hydrophobic partition dominated adsorption on resins with linearity of PFOS.

Among five resins, PFA300 gave the highest capacity of adsorption for both PFOS and PFOA (455 and 115 mg/g). Because PFA300 had high ion exchange capacity (1.4 eq/L) it was categorized as type II. Type II was a quaternary ammonium functional group which had one of the methyl groups ($-CH_3$) of type I was replaced with ethanol group ($-C_2H_4OH$). It has been noticed that type II had a slightly greater adsorption

capacity than type I (Crittenden *et al*., 2005). Therefore, functional groups of resins influenced adsorption of PFOS and PFOA.

In comparing K_f value from *Freundlich* equation with other adsorbents, PFA300 had higher adsorption capacity than GAC (60.9 mg/g for PFOS and 11.8 mg/g for PFOA), Zeolite (0.7 mg/g for PFOS) (Ochoa-Herrera and Alvarez, 2008), ash (26.8 mg/g for PFOS) (Chen *et al*., 2011) and non-ion exchange resin Dow L493 (65.9 mg/g for PFOA) (Senevirathna *et al*., 2011). The high adsorption capacities indicated that the resins are very effective for PFOS and PFOA removal from wastewater especially, PFA300.

Furthermore, distribution coefficient (K_d) between solid phase and dissolved phase in the adsorption isotherm experiments were calculated by **Eq. (4.3)**, which is the ratio of the PFOS or PFOA on solid phase (C_s, mg/g) to PFOS and PFOA in dissolved phase (C_w, mg/L).

$$K_d = \frac{C_s}{C_w} \tag{4.3}$$

The larger K_d value indicates higher amount of PFOS and PFOA was adsorbed on solid phase. From the adsorption isotherm, it was observed that K_d values of PFOS were in the range of 77 – 1,146 L/g whereas PFOA were in much lower range (13 - 242 L/g). Based on K_d value, it can be concluded that PFOS has higher affinity to resins than PFOA. The K_d value of PFOS adsorption by anion exchange resins was found to be higher compared to other adsorbent materials such as mineral surfaces (Johnson *et al*., 2007), ash, chars, and carbon (Chen *et al*., 2011). Additionally, K_d values of PFOA in this study were found to be higher than activated sludge (Zhou *et al*., 2010). The high affinities of PFOS and PFOA to the resins were effective to adsorb these compounds onto the surface of adsorbents.

4.4.3 Resins properties on adsorption of PFOS and PFOA

Removal efficiencies were calculated from adsorption isotherm experiments at 1 mg/L of PFOS and PFOA and the values are showed in **Table 4.6**. As mentioned above, the functional group influenced on adsorption of PFOS and PFOA onto resins. Therefore, PFA300 showed higher removal efficiency than other resins.

Table 4.6 Properties of anion exchange resins

Adsorbents	Removal efficiency PFOS (%)	Removal efficiency PFOA (%)	Functional group	Diameter (mm)	Ion exchange capacity (eq/L)	Swelling (%)	Moisture retention capacity (%)
PFA300	81	58	R-$(CH_3)_2(C_2H_4OH)N^+$ (Type II)	0.56	1.4	10	43
Dow Marathon A	79	54	R-$(CH_3)_3N^+$ (Type I)	0.58	1.3	20	55
PFA400	53	36		0.57	1.3	20	53
PFA444	43	34		0.57	1.1	25	58

Table 4.7 Correlation coefficient of resins properties and removal efficiency of PFOS and PFOA

Parameters	PFOS	PFOA
Diameter (mm)	-0.04	-0.11
Ion exchange capacity (eq/L)	0.82	0.76
Swelling (%)	-0.77	-0.78
Moisture retention capacity (%)	-0.66	-0.68

The properties of anion exchange resins were gathered from manufacturers. Based on availability of data, properties of resin such as diameter, ion exchange capacity (eq/L), swelling (%) and moisture retention capacity (%), were correlated with removal efficiency of PFOS and PFOA, as shown in **Table 4.7**. Diameter was found to have no effect on adsorption capacity of PFOS and PFOA onto resins. Ion exchange capacity (eq/L) showed positive correlation coefficient. Swelling (%) and moisture retention

capacity (%) showed negative correlation with removal efficiency of PFOS and PFOA. Therefore, it can be deduced that high swelling (%) and moisture retention (%) decreased the adsorption capacity of resin. Due to high moisture, the active group was surrounded by water and also it filled the voids in the resin matrix. Thus, high moisture content of resin has less dry mass, thus less active groups and lower adsorption capacity (Dale and Irving, 2007; François de Dardel, 2010).

4.4.4 Adsorption isotherms of PFOS and PFOA by GAC

GAC is commonly used as adsorbent to remove organic compounds in water. It has been identified that F400 (coal based) is the best type of GAC to eliminate PFOS (Ochoa-Herrera and Sierra-Alvarez, 2008). Similar type of GAC was used in this experiment with the physical properties as described in Section 4.3.2. GAC has heterogeneous adsorption site than anion exchange resins. More than 78% total pore volume in GAC is occupied by micropores, 14% mesopores and the rest is occupied by macropores. GAC was found to have less adsorption capacity (K_f) compared to anion exchange resins as reported in this study, except PFA400 and PFA444 for PFOS and IRA400 for PFOA.

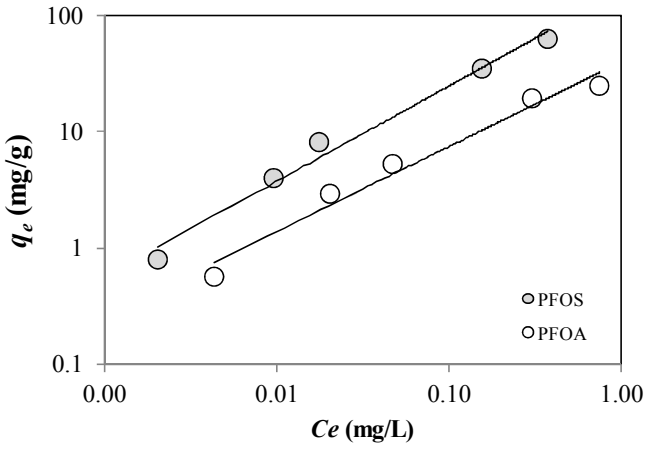


Figure 4.3 Isotherm of GAC adsorption of PFOS and PFOA

Figure 4.3 shows adsorbed amount of PFOS and PFOA onto GAC at equilibrium concentration were 163 and 40 mg/g, respectively. Among adsorbents tested in this

study, GAC's adsorption capacities were found to be lower than other adsorbents. It has been reported by Schaefer (2006) that the application of GAC to eliminate PFOS has failed in German drinking water treatment plants.

4.4.4 Adsorption isotherms of single PFC onto PFA300

Among tested adsorbents in this study, PFA300 had higher performance adsorption than others. Thus, PFA300 was selected to test with eight PFC (PFBuS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA and PFOA). **Figure 4.4** shows K_f of eight PFC isotherms adsorbed onto PFA300. In order to compare different behavior of PFCs with carbon chain length, values of K_f for PFC isotherms in ultrapure water were plotted by length of PFC carbon chains of two PFCs groups (PFASs and PFCAs). Values of K_f in *Freundlich* equation indicate adsorption capacities of PFCs onto PFA300.

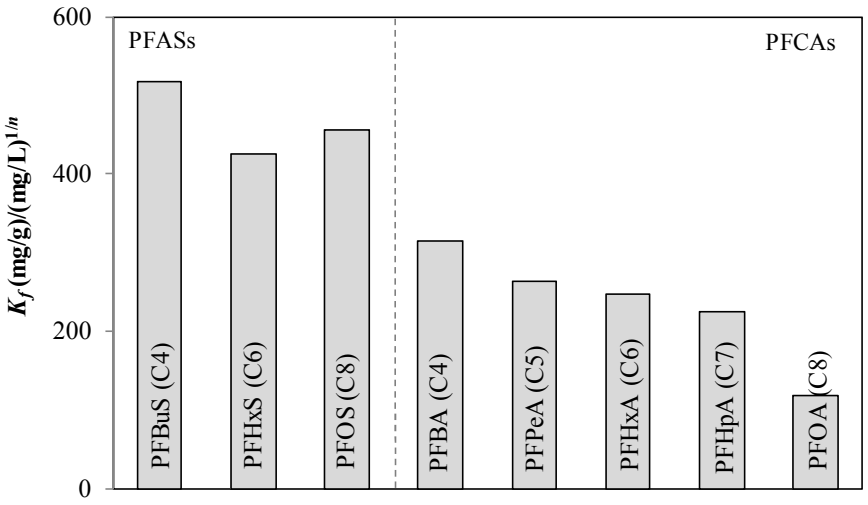


Figure 4.4 Adsorption capacities of eight PFC adsorbed onto PFA300

K_f value increased with decreasing carbon chain length for PFASs (C4, C6, and C8) and PFCAs (C4 - C8) which showed that shorter chained PFCs were easier to be adsorbed onto PFA300. This tendency can be explained by the properties of PFCs and PFA300. Shorter chain PFCs have more hydrophilic properties than longer ones which can easily be diffused into pores of adsorbents. Additionally, PFA300 has hydrophilic properties

because it contains ethyl alcohol in its functional group. Similar result was reported by Deng *et al*. (2010). They found that IRA410 (anion exchange resin which contained one –OH group) adsorbed much higher amount of PFBuS (C4) than PFOS (C8).

4.4.6 Comparative adsorption of mixed eleven PFCs onto PFA300

Mixed eleven PFCs was used to study adsorption behavior onto PFA300. Many PFCs may simultaneously present in wastewater, and their adsorption behavior and mechanism onto the PFA300 may be different. To illustrate the possible adsorption mechanisms of PFCs, different perfluorocarbon chain lengths and functional groups were compared and presented in this study. **Figure 4.5** shows adsorption capacities (K_f) of mixed PFCs which are PFBuS (C4), PFHxS (C6), PFOS (C8), PFPeA (C5), PFHxA (C6), PFHpA (C7), PFOA (C8), PFNA (C9), PFDA (C10), PFUnDA (C11) and PFDoDA (C12) onto PFA300.

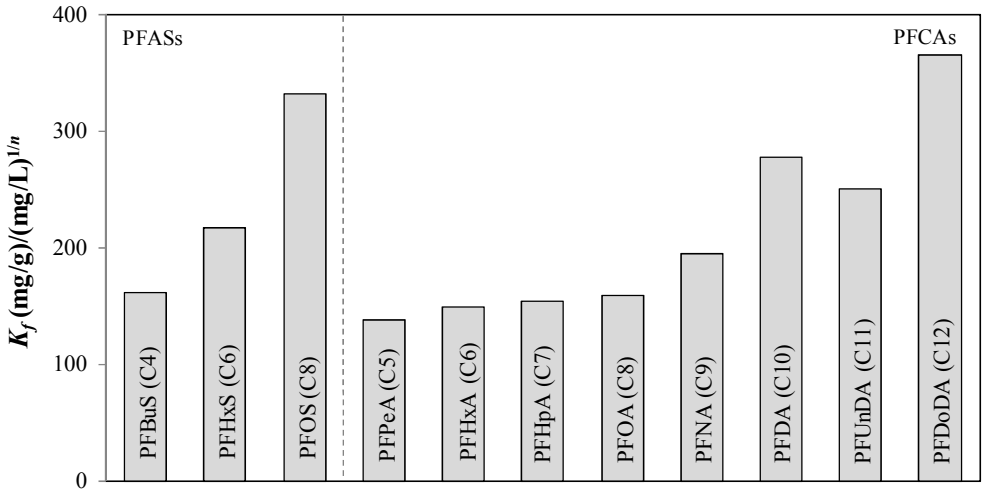


Figure 4.5 Adsorption capacities of mixed eleven PFCs adsorbed onto PFA300

In PFASs group, PFOS was more adsorbed onto PFA300 than PFBuS and PFHxS. In PFCAs group, PFDoDA was the highest adsorbed onto PFA300 followed by PFUnDA, PFDA, PFNA PFOA, PFHpA, PFHxA, and PFPeA. It was found that adsorption capacity increased with the increase of the C-F length. Perfluorinated sulfonates were

higher adsorbed than that of the corresponding perfluorinated carboxylate with the same number of carbons, which were related to the more hydrophobic property of perfluorinated sulfonates. This result was completely opposite in comparison with that of single PFC (in section 4.4.4) due to the competition of each PFC in mixed solution onto adsorption sites. Longer chains have more hydrophobicity which first adsorbed on adsorbent and followed by shorter chains. Mixed PFCs system was related to their hydrophobic C-F chains, and hydrophobic interaction played an important role in the adsorption process.

To further understand, **Figure 4.6** rearranged some of data from **Figure 4.5** to compare effect of PFCs chain length. **Figure 4.6** shows the comparative adsorption of PFCs with same No. of carbons and No. of perfluorocarbons (C-F). PFHxA (C6) and PFHxS (C6) are the same number of carbons while PFHxS (C6) and PFHpA (C7) are the same number of perfluorocarbons. In addition, a similar pattern was compared in PFOA (C8), PFOS (C8) and PFNA (C9). It can be seen that the adsorption capacities of PFHxS and PFOS were higher in those PFCs.

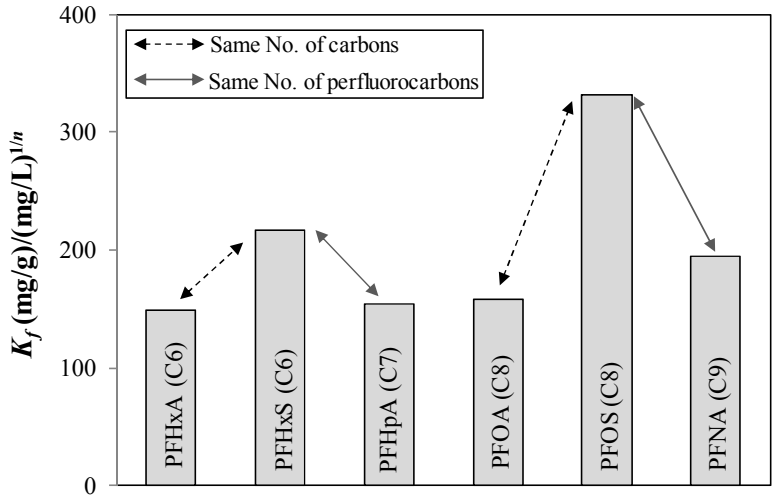


Figure 4.6 Comparative adsorption of mixed PFCs with same No. of carbons and No. of perfluorocarbons

With same number of carbons, it was found that the adsorption capacity of sulfonate compounds in PFHxS (C6) - PFHxA (C6) and PFOS (C8) - PFOA (C8) were higher than carboxylic compounds. The sulfonate group was more strongly adsorbed onto adsorbent than carboxylic group.

Although they have same number of carbons (PFHxA - PFHxS and PFOA - PFOS), perfluorinated sulfonates have one more carbon chain (longer C-F chain) than perfluorinated carboxylates, showing stronger hydrophobicity. At the same number of perfluorocarbon chain (PFHxS – PFHpA and PFOS – PFNA) also found that sulfonate group was more adsorbed onto adsorbents than carboxylate group. Evidently, the adsorption capacities of mixed PFCs on PFA300 were related to their hydrophobic C-F chain and functional groups of compounds.

4.4.7 Effects of temperature on adsorption

The effects of temperature on the adsorption of PFOS and PFOA are shown in **Fig. 4.7**. The temperature was varied from 10 to 50°C. It can be seen that PFOS was slightly more adsorbed than PFOA as a result of hydrophobic properties of PFOS.

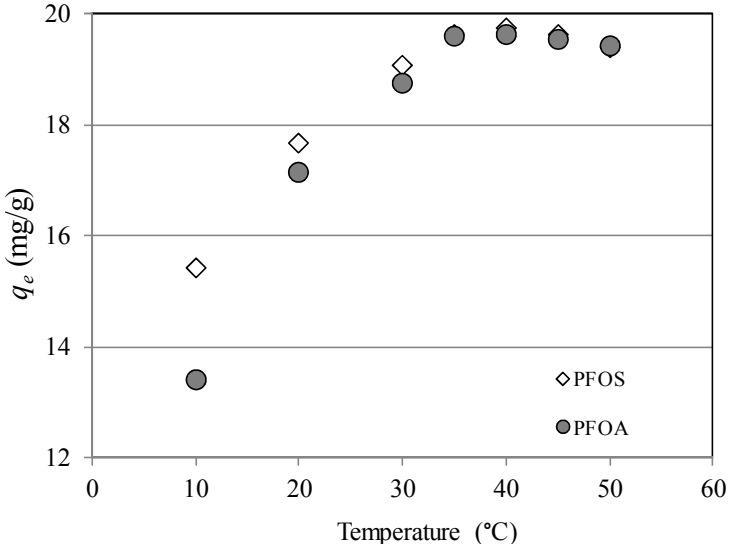


Figure 4.7 Effects of temperature on the adsorption of PFOS and PFOA onto PFA300

When temperatures increased from 10 to 40°C, adsorbed amount of PFOS and PFOA also increased. This is due to the fact that the increase of the temperature accelerates the diffusion of PFOS and PFOA molecules into pores and enhances to the active sites on adsorbent. Thus, the adsorption increases with increasing temperature.

The decreasing adsorption of PFOS and PFOA when increasing temperature from 40 to 50°C is mainly due to two effects. One is the solubility of PFOS and PFOA which increases with temperature, which reduces hydrophobic interactions. The other effect is the increase in vibrational energy of the adsorbed PFOS and PFOA molecules at higher temperatures, so that more PFOS and PFOA molecules have sufficient energy to overcome the attractive force and desorb back into solution. Similar studies have reported that PFOA has high adsorption onto powdered activated carbon (PAC) at 40°C (Qu *et al*., 2009).

4.4.8 Effects of pH on adsorption

In general, PFOS and PFOA were adsorbed at lower pH due to protonation of adsorbent surface (*i.e.* GAC and PAC) which enhanced the electrostatic interaction of anionic compounds on the surface. **Figure 4.8** shows the effects of pH on the adsorption of PFOS and PFOA onto PFA300. Solution pH was adjusted with 0.1 M NaOH and 0.1 M HCl which was varied from 3 to 10 in pH scale. The results were not very different between PFOS and PFOA. It was found that the adsorbed amount of PFOS and PFOA decreased with the increase in pH of solution because PFOS and PFOA have low pK_a (-3.27 for PFOS and 2.5 for PFOA) (Brooke *et al*., 2004; Goss, 2008; Steinle-Darling and Reinhard, 2008; Park *et al*., 2009) and they exist as anions in solution in the pH range studied. The results show that the solution pH had a slightly greater effect on PFOA adsorption than on PFOS adsorption.

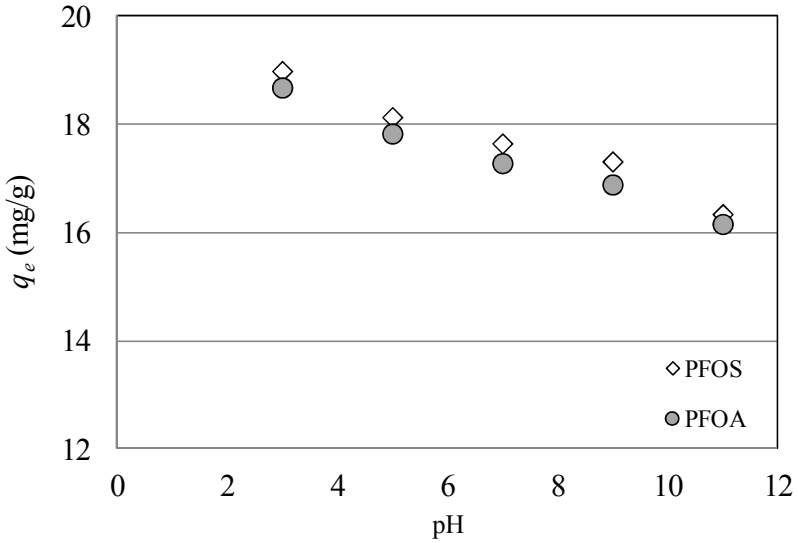


Figure 4.8 Effects of solution pH on the adsorption of PFOS and PFOA onto PFA300

Some of PFOA molecules could be existed in neutral form at pH 3 because it is very close to pK_a of PFOA. However, PFOS still exist in anionic form. Another possible reason is that at low pH, resin could be protonated, and the electrostatic attraction facilitated the adsorption process. Thus, the increased PFOS and PFOA adsorption at lower pH is likely promoted by enhanced electrostatic attraction (Johnson *et al*., 2007).

4.4.9 Effects of ionic strength on adsorption

Ionic strength is the concentration of ionic charge in solution (a liquid with positive and negatively charged ions dissolved in it). Effect of ionic strength was carried out by batch experiment. PFOA (1 mg/L) was used in this study. Ionic strength was prepared from NaCl at 0.1, 1, 10, 100, and 1000 mM. **Figure 4.9** shows the effects of ionic strength on adsorption of PFOA onto PFA300. Adsorption of PFOA decreased when ionic strength increased from 0.1 to 1000 mM. The reasons are electrostatic repulsion and suppression of the dlectrostatic attraction at higher ionic strength. Background electrolyte concentrations of 0.1 mM showed the highest adsorption of PFOA. Increased ionic strenght resulted in reducing PFOA adsorption. Basically, anion exchange resin can not be applied to high ionic water or wastewater.

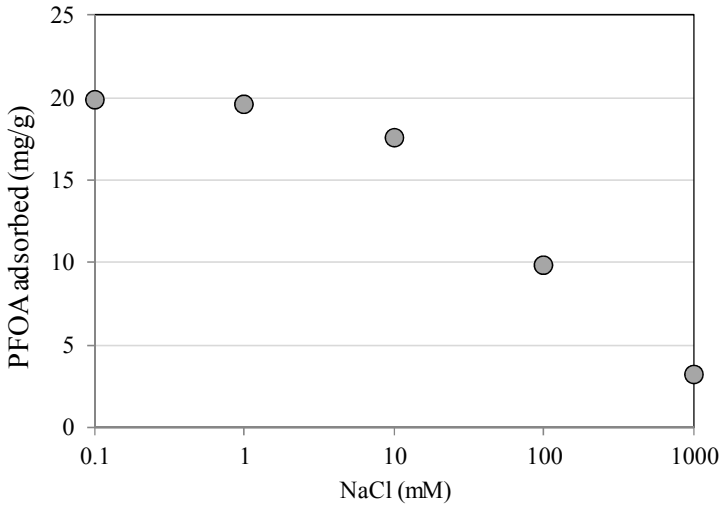


Figure 4.9 Effects of ionic strength on PFOA adsorption onto PFA300

4.5 Summary

1. Most anion exchange resins in this study were more effective for removal of PFCs than GAC, especially PFA300 has the highest adsorption capacity 455 mg/g for PFOS and 117 mg/g for PFOA. PFA300 has ethyl alcohol in its functional group which influenced on adsorption rate and capacity.
2. PFOS was more adsorbed onto adsorbents than PFOA which can be explained by influence of hydrophobic and functional groups of compounds.
3. Shorter chain PFCs (more hydrophilic properties) diffused into ion exchange site while in mixed PFCs condition, hydrophobic interaction of long chain PFCs played an important role.
4. PFOS and PFOA were highly adsorbed at 35 - 40°C, lower pH (3) and low ionic strength (0.1 M) as the results showed the increase in the PFCs adsorption alongside with the decrease in pH. Likewise, the decrease in the ionic strength favors the higher adsorption of PFOA on PFA300.
5. In this study, PFA300 was recognized to be the suitable adsorbent for removal of PFCs which was used for regeneration studies and column experiments in next Chapters.

Chapter 5

Regeneration and reusability by batch experiments

5.1 Introduction

In Chapter 4, it showed that anion exchange resins were effective adsorbents, which had high capacity to adsorb PFCs in ultrapure water. When the resin saturated, regeneration process will be conducted to reactivate resin. In the case of synthetic resins, there is a possibility to regenerate the materials onsite, which is one of the main advantages over conventional GAC filters. In the case of GAC, normally regeneration is done at a separate plant (offside). Carbon regeneration is accomplished primarily by thermal means. Organic matter within the pores of the carbon is oxidized and thus removed from the carbon surface. Approximately 5 to 10 percent of the carbon are destroyed in the regeneration process or lost during transport and must be replaced with virgin carbon. The capacity of the regenerated carbon is slightly less than that of virgin carbon. Repeated regeneration degrades the carbon particles until equilibrium is reached eventually providing predictable long term system performance.

One of the major advantages of these resins over GAC is their onsite regenerability through steam stripping, solvent extraction and microwave irradiation. The ability to regenerate resins onsite potentially offers economic advantages over GAC, which typically requires offsite high temperature incineration for regeneration. Since, the resins can be regenerated; the water/wastewater treatment process using resins is economical. Solvent regeneration was selected in this study. Solvent regeneration, a solvent in which the adsorbate is highly soluble, is passed through the saturated adsorbent.

This chapter focused on the major PFCs as PFOS. Generally, anion exchange resins are regenerated by high concentration of NaCl and NaOH. However, Deng *et al*. (2010)

reported high concentration of NaCl and NaOH could not desorb PFOS adsorbed on resin. Therefore, the suitable regeneration solution for PFOS adsorbed on resin should be studied. Moreover, there is no information about reusability of regenerated resin use for PFOS and PFOA removal. Therefore, the results reported here are important in complementing new information to this research topic.

5.2 Objectives

The objectives of this study were

1. To study the suitable regeneration solutions of selected resin after treating PFOS
2. To investigate the regeneration rate of selected resin and GAC after treating PFOS
3. To evaluate the reusability of regenerated resin for PFOS removal
4. To investigate the regeneration efficiency of used resin from wastewater contained PFOA

5.3 Methodology

5.3.1 Sample preparation: PFOS or PFOA adsorption

Pre-washed and dried of adsorbents were done as described in Section 4.3.1, Chapter 4. Adsorbents were prepared for regeneration study by placing 2 mg of adsorbent into 15 mL of PP tube together with 10 mL of PFOS or PFOA (10 mg/L) and shaken for 48 hours by thermo shaker at 120 rpm and 25ºC.

After 48 hours, adsorbent and solution were immediately separated. The solution was measured remaining of PFOS or PFOA concentration. Adsorbents were washed with ultrapure water and methanol to remove remaining of PFOS or PFOA. Then, they were washed with ultrapure water to remove remaining of methanol. GAC does not require to be washed with methanol because PFOS or PFOA adsorbed on GAC could be desorbed into methanol. Therefore, GAC was washed with ultrapure water (5 mL x 6 times). Adsorbents were used for regeneration study in next experiments. Procedure of sample preparation is shown in **Fig. 5.1**.

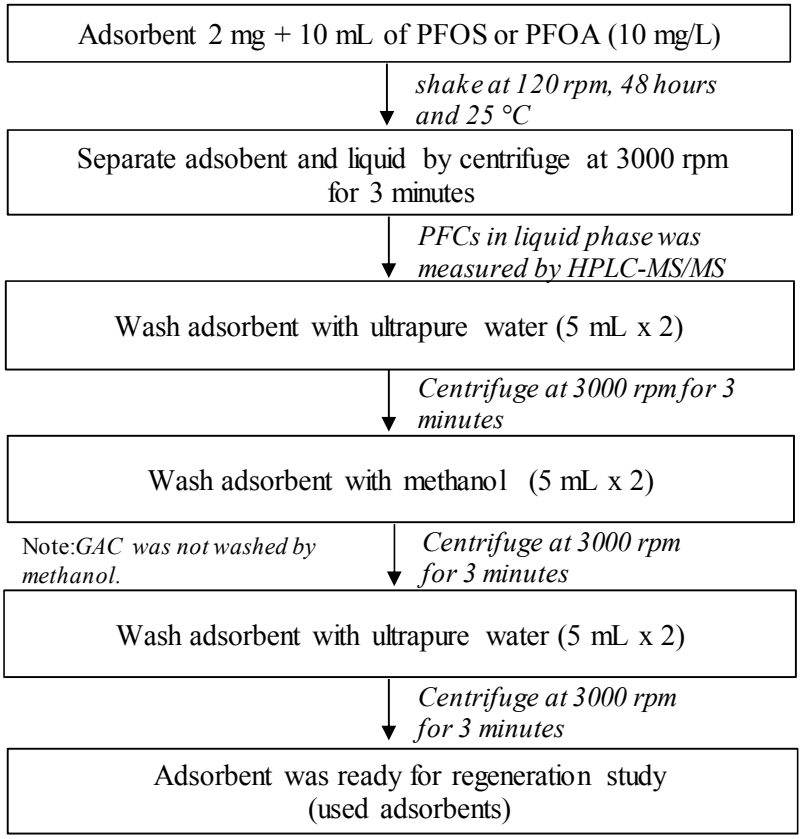


Figure 5.1 Procedure of sample preparation of PFOS and PFOA adsorption

5.3.2 Regeneration solutions of selected resin

PFA300 was selected for studying regeneration because it has the highest performance on PFOS and PFOA adsorption out of five anion exchange resins in Chapter 4. Moreover, PFA300 was anion exchange type II, which have been reported high regeneration efficiency. In this study, solvent washing technique was utilized because it can be done onsite, require less energy and can be conducted in room temperature.

In general, high concentration solutions of NaCl and NaOH are commonly used to regenerate used anion exchange resin. PFOS has hydrophobic properties which highly dissolved in organic solvents such as methanol, ethanol, hexane, acetone and dimethyl sulfoxide (DMSO) (3M, 2001). Thus, NaCl, NaOH and methanol were used as

regeneration solutions for regeneration of PFA300. Previous study reported that 1% NaCl and 1% NaOH in 70% methanol were effective to regenerate IRA67 resin after PFOS adsorption (Deng *et al*., 2010). Therefore, the ratio of methanol/ultrapure water (7:3) was used in this study while the concentrations of NaCl and NaOH were varied.

Various types of regeneration solutions were used for regeneration of PFA300 which were 100% methanol, 1% NaOH, 5% NaOH, 1% NaCl, 5% NaCl, 1% NaOH in methanol/ultrapure water (7:3), 3% NaOH in methanol/ultrapure water (7:3), 5% NaOH in methanol/ultrapure water (7:3), 1% NaCl in methanol/ultrapure water (7:3), 3% NaCl in methanol/ultrapure water (7:3) and 5% NaCl in methanol/ultrapure water (7:3). PFA300 had been prepared in Section 5.3.1 was regenerated by adding 10 mL of each solution. Thermo shaker was set at 120 rpm, 25ºC for 48 hours. Then, PFOS concentration in aqueous solution was analyzed by HPLC-MS/MS.

5.3.3 Regeneration rate of selected resin

The mixtures of NaCl and NaOH in methanol/ultrapure water (7:3) solution were selected to study on regeneration of PFA300 with different contact. Regeneration solutions (10 mL) were shaken together with PFA300 that had been prepared in Section 5.3.1. Samples were collected at different interval times (0, 1, 2, 4, 8, and 12 hours) as shown in **Table 5.1**. All samples were diluted into 40% acetonitrile in ultrapure water and analyzed by HPLC-MS/MS. Finally, regeneration percentages were calculated (n = 5). Regeneration rate was calculated as shown in **Eq. (5.2)**.

$$Regeneration\ percentage\ (\%) = \frac{E_i}{E_0}\ x\ 100 \qquad (5.2)$$

Where E_i = PFOS concentration (mg/L) in liquid phase at time intervals i

E_0 = Initial PFOS concentration (mg/L) used in the adsorption experiment

5.3.4 Regeneration rate of GAC

The regeneration of GAC by solvent washing technique was examined. GAC prepared in Section 5.3.1 was used in this experiment. Pure methanol was used as regeneration

solution. Ten mL of methanol was added and shaken together with GAC. Samples were collected at different interval time (0, 1, 2, 4, 8, 12, 24, and 48 hours). All samples were analyzed by HPLC-MS/MS.

5.3.5 Reusability of selected resin

To test reusability of resin, an experiment was conducted by washing the regenerated PFA300 with ultrapure water and methanol to remove remaining PFOS. Then it was washed with ultrapure water to remove methanol remaining. PFA300 was then reused as the adsorbent for a 10 mL solution of PFOS at a concentration of 10 mg/L. The regeneration and reuse cycles were repeated for up to six cycles. The reusability procedure is shown in **Fig. 5.2**.

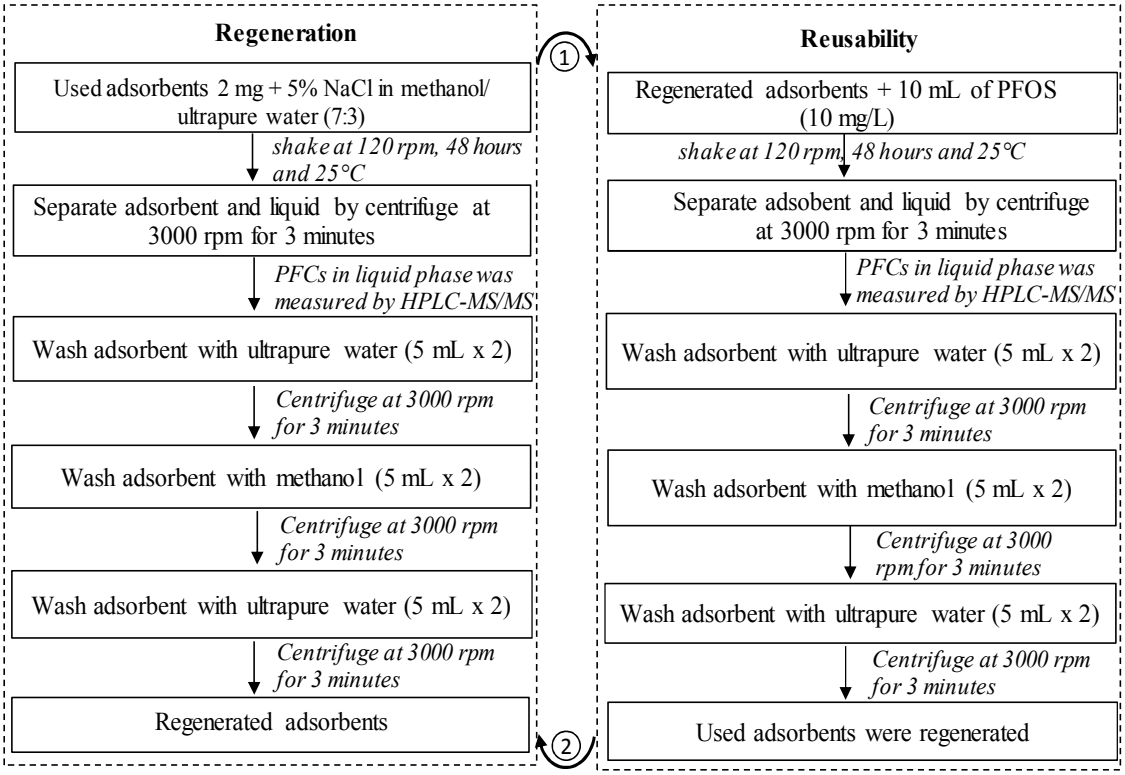


Figure 5.2 Scheme of reusability experiment

After that adsorbents were washed with ultrapure water, methanol and again with ultrapure water. Regeneration was conducted by using 5% NaCl in methanol/ultrapure water (7:3). Adsorbents were shaken with 10 mL of 5% NaCl in methanol/ultrapure water (7:3) for 48 hours. Shaker condition was set at 120 rpm, 25 ºC. All samples were diluted into 40% acetonitrile in ultrapure water and analyzed by HPLC-MS/MS. Finally, regeneration percentages were calculated.

5.3.6 Regeneration of resin used for PFOA removal in wastewater

The experiments were conducted both with ultrapure water and wastewater. PFOA (10 mg/L) was prepared in ultrapure water. Effluent of a wastewater treatment system containing PFOA was collected and used in this experiment. The initial pH was 7.0 and TOC was 9.4 mg/L. The initial PFOA concentration in wastewater was 220 ng/L. Wastewater was spiked by stock solution of PFOA which was prepared in ultrapure water, so final concentration was 10 mg/L. Sample preparation was conducted similar process in Section 5.3.1 for both adsorption of PFOA in ultrapure water and wastewater before regeneration. Remaining PFOA in solution was measured by HPLC-MS/MS after adsorption process.

5.4 Results and discussion

5.4.1 Regeneration solutions of selected resin

More value is added to the benefit of using adsorbent if there is possibility of regeneration of the resin after reaching its capacity. Thus, solvent washing technique was applied on the selected resin to conduct the regeneration study. This technique is convenient and can be done on-site. Regeneration of anion exchange resins occurred by ion exchange process. Adsorbed PFOS on resins were replaced by anion from regeneration solutions to reactivate resin.

Table 5.1 Summary of experimental conditions in this study

Experiments	PFCs	Adsorbent	Amount of adsorbent (mg)	Volumn of sample (mL)	Shaking condition	Type of regeneration solution
Regeneration solution	PFOS	PFA300	2	10	120 rpm, 25 °C at 48 hours	100% MeOH, 1% NaOH, 5% NaOH, 1% NaCl, 5% NaCl, 1% NaOH in MeOH/ultrapure water (7:3), 5% NaOH in MeOH/ultrapure water (7:3), 1% NaCl in MeOH/ultrapure water (7:3), and 5% NaCl in MeOH/ultrapure water (7:3)
Regeneration rate	PFOS	PFA300			120 rpm, 25 °C at 1, 2, 4, 8 and 12 hours	1% NaOH in MeOH/ultrapure water (7:3), 3% NaOH in MeOH/ultrapure water (7:3), 5% NaOH in MeOH/ultrapure water (7:3), 1% NaCl in MeOH/ultrapure water (7:3), 3% NaCl in MeOH/ultrapure water (7:3) and 5% NaCl in MeOH/ultrapure water (7:3),
Regerneration of GAC	PFOS	GAC	2	10	120 rpm, 25 °C at 1, 2, 4, 8 12, 24 and 48 hours	100% Methanol
Reusability (n = 5)	PFOS	PFA300	2	10	120 rpm, 25 °C at 48 hours	5% NaCl in MeOH/ultrapure water (7:3)
Regeneration of used adsorbent in removal of PFOA in wastewater	PFOA	PFA300	2	10	120 rpm, 25 °C at 48 hours	5% NaCl in MeOH/ultrapure water (7:3)

Note: MeOH is methanol

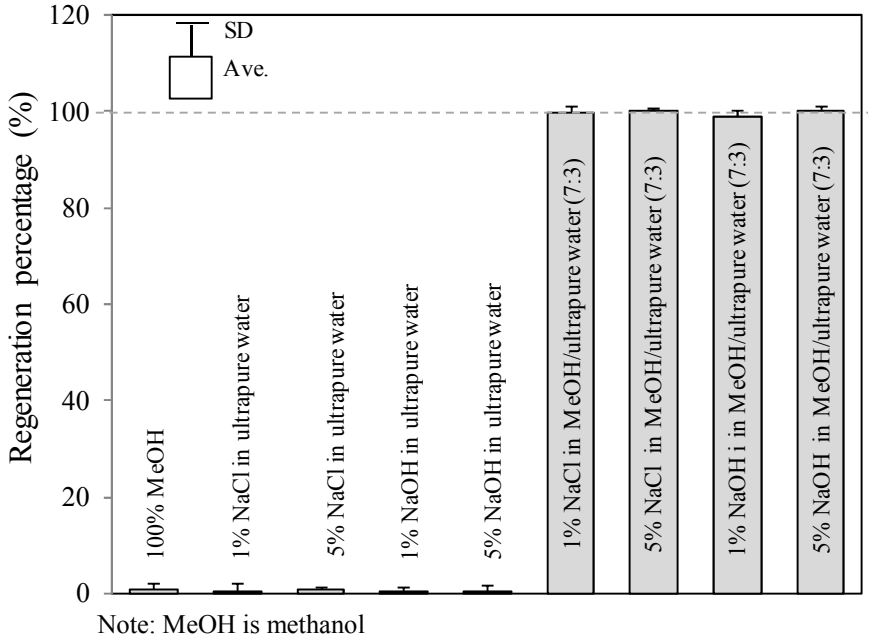
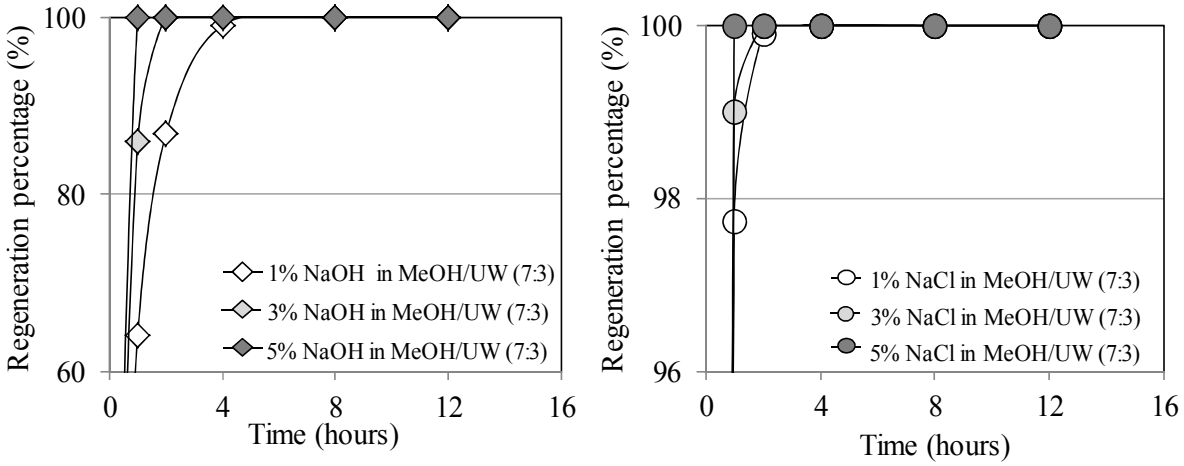


Figure 5.3 Regeneration percentage of PFA300 by different regeneration solutions.

Figure 5.3 shows different types of solutions for regeneration of PFA300. The results showed that solutions of NaCl, NaOH and methanol were unable to regenerate PFA300. Though, concentration of NaCl and NaOH (in 100% ultrapure water) was increased from 1% to 5%, they were not effective for desorbing PFOS from PFA300 because PFOS has low water solubility at high salt concentration and ionic strength (Brooke *et al*., 2004). In case of pure methanol, PFOS was unable to directly desorb into methanol. Thus, mixed solutions of NaOH or NaCl in methanol/ultrapure water (7:3) were applied in this study. Each concentration of 1% NaCl, 5% NaCl, 1% NaOH and 5% NaOH was mixed in methanol/ultrapure water (7:3) which were used for resin regeneration. Adsorbed PFOS was first desorbed from binding site on the surface of resin and then dissolved in methanol. After shaking for 48 hours, it was found that the regeneration efficiency increased more than 99% for all solutions. The solubility of PFOS enhances after mixing with methanol. Therefore, the solutions of NaCl and NaOH in methanol/ultrapure water (7:3) were suitable for PFA300 regeneration.

5.4.2 Regeneration rate of selected resin

Regeneration rate of PFA300 was investigated. **Figure 5.4** shows regeneration rate of PFA300 using different regeneration solutions at different interval time. The solutions of NaCl and NaOH in methanol/ultrapure water (7:3) were highly effective for regeneration of PFA300 in this study. The regeneration rate increased with increasing concentration of NaCl and NaOH. It was found that at one hour shaking time, 1% NaCl in methanol/ultrapure water (7:3) showed regeneration efficiency more than 97% and it was 64% with 1% NaOH in methanol/ultrapure water (7:3). Chloride has higher ion selectivity than hydroxide ($Cl^- > OH^-$), so NaCl solution desorbed PFOS faster than NaOH solution. When the percentage of NaOH increased from 1% to 3%, the regeneration efficiency also increased from 64% to 86% respectively. Finally, when NaOH increased up to 5%, the regeneration efficiency was more than 99% at one hour shaking time. After four hours, all regeneration solutions desorbed PFOS completely. However, 5% NaCl in methanol/ultrapure water (7:3) was the most effective solution due to the fastest of regeneration rate.



Note: MeOH is methanol and UW is ultrapure water

Figure 5.4 Regeneration percentage of the used PFA300 on PFOS adsorbed

5.4.3 Regeneration rate of GAC

In this study, pure methanol was used for regeneration of GAC. GAC could regenerate only 37% at 48 hours as shown in **Fig. 5.5**. It was difficult to regenerate GAC using organic solvent (100% methanol) at normal condition due to strong interaction between PFOS and GAC surface. PFOS has a long chain of C-F having hydrophobic properties. Nemethy and Scherage (1962) reported that hydrophobic compounds adsorbed more strongly on carbon. Moreover, another possible reason is pore diffusion. PFOS could have diffused into deep pores of GAC, therefore it is difficult and time consuming for desorbing PFOS into an organic solvent. Similar results have been reported by Senevirathna *et al*. (2010) that PFOS recovery percentage of GAC was 40% after 270 minutes. Adsorption of PFOS on a resin occurred by ion exchange and adsorption on the outer surface of the resin. This may be a reason for the faster regeneration of resin than GAC. Based on the result, it was easy to regenerate PFA300 and more feasible for in-situ regeneration than GAC.

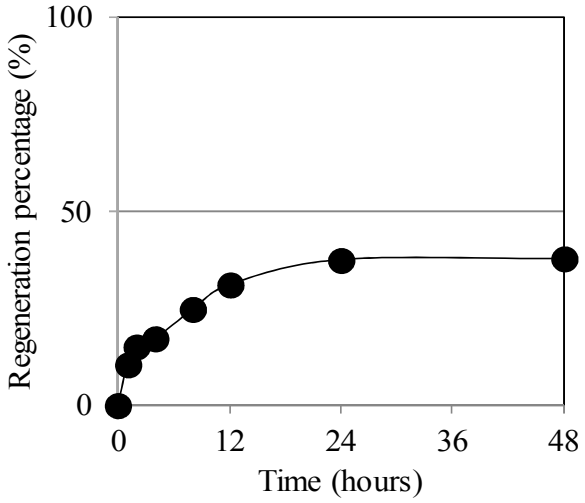


Figure 5.5 Regeneration rate of GAC after treating PFOS

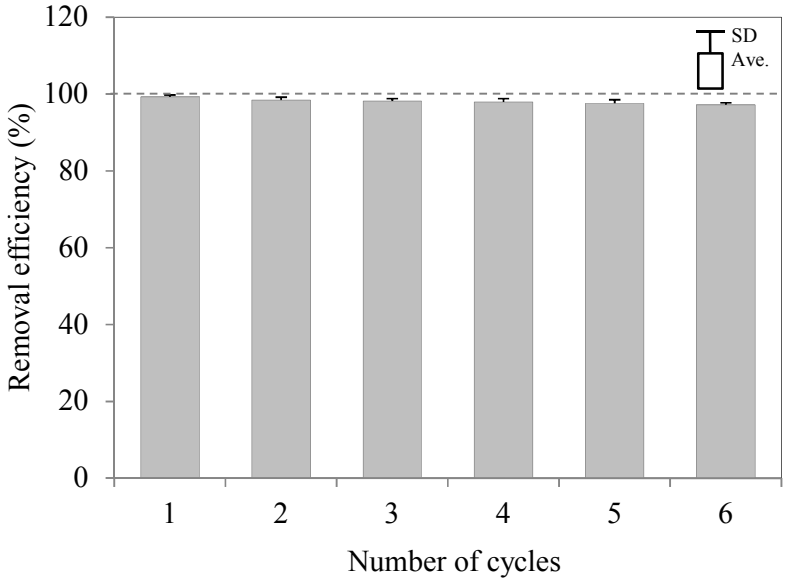


Figure 5.6 Reusability efficiency of PFA300 by using 5% NaCl in methanol/ultrapure water (7:3) for regeneration

5.4.4 Reusability of selected resin

In this experiment, 5% NaCl in methanol/ultrapure water (7:3) was selected, since it showed the fastest rate for PFA300 regeneration. The performance of regenerated PFA300 on removal of PFOS was investigated up to six cycles. **Figure 5.6** shows the reusability efficiency of PFA300 on adsorption of PFOS. The first cycle obtained the highest removal efficiency (more than 99%) since its fresh adsorbent. The removal efficiency slightly dropped from 99% to 97% in subsequent cycles. Since it still showed high removal efficiency up to six cycles, PFA300 has a high potential of reusability.

5.4.5 Regeneration of resin used in PFOA removal in wastewater

When adsorbent is applied to water/wastewater, the ability to regenerate a resin onsite is a key factor in determining the economics of a resin. 5% NaCl in methanol/ultrapure water (7:3) was effective for regeneration of PFOS adsorbed onto resin. PFOS and PFOA are anionic surfactants and have almost similar properties such as strong water

and oil repellency, chemical and thermal stability. Thus, the similar regeneration solution was applied in this experiment. Regeneration experiments of used PFA300 for PFOA removal in industrial wastewater were investigated. The regeneration efficiencies were compared between regeneration of used PFA300 for PFOA removal in ultrapure water and industrial wastewater.

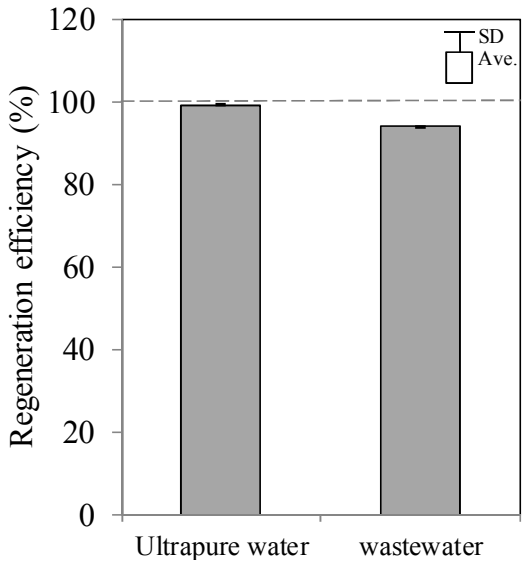


Figure 5.7 Regeneration percentage of used resin in removal of PFOA from ultrapure water and wastewater

Figure 5.7 shows that the regeneration percentage of used resin in the removal of PFOA from ultrapure water was higher than in wastewater. It was 99% in ultrapure water, while in wastewater was 94%. Used resin in industrial wastewater had lower regeneration percentage that may cause from matrix interferences in wastewater which could be obstructing for releasing of PFOA from resin.

5.5 Summary

1. PFA300 was also successfully regenerated by NaOH and NaCl in methanol/ultrapure water (7:3). The solution of NaCl in methanol/ultrapure water (7:3) showed faster regeneration rate than NaOH in methanol/ultrapure water (7:3)

because chloride has higher ion selectivity than hydroxide ($Cl^- > OH^-$), so NaCl solution desorbed PFOS faster than NaOH solution.

2. PFA300 was regenerated by 5% NaCl in methanol/ultrapure water (7:3) and it was reused for PFOS removal (more than 97%) for up to six cycles.
3. The regeneration percentage slightly reduced when PFA300 applied to in industrial wastewater that may cause from matrix interferences in wastewater.
4. Regeneration of used adsorbents in column experiments were examined in Chapter 6 and 7.

Chapter 6

Column experiments for removal of PFOS and PFOA

6.1 Introduction

Adsorption technique has been widely used for treatment of industrial wastewater, which is effective and economical technique for treatment of huge amount of wastewater. Activated carbon was often used in water/wastewater treatment. Granular activated carbon (GAC) was reported that it saturated at a faster rate. Senevirathna *et al.* (2010) found that GAC had a faster breakthrough than non-ion exchange resins (Dow V493, Dow L493 and XAD4). A water treatment plant in Germany also reported poor performance of activated carbon for elimination of PFCs (Schaefer *et al*., 2006). These results suggested that current water/wastewater treatment were not effective for the removal PFOS and PFOA.

Previous chapters show that anion exchange resins have high removal performance as well as benefit of regeneration. Although in general practice, resins are used in column mode, most researches focus only on the batch adsorption mode, therefore the results of this study are important for implementing PFOS and PFOA removal from the practicality prospective. Moreover, the column studies were conducted at trace PFOS and PFOA level, which is close to its real level detected in water and wastewater.

6.2 Objectives

1. To investigate continuous removal of PFOS using anion exchange resins and GAC in column experiments in synthetic water
2. To investigate continuous removal of PFOA using anion exchange resins, non- ion exchange resin and GAC in column experiments in synthetic water

3. To investigate regeneration percentage of adsorbents from column adsorption of PFOS (by batch experiments).
4. To investigate regeneration percentage of adsorbents from column adsorption of PFOA (by column experiments)

6.3 Methodology

The adsorption process on removal of PFOS and PFOA from synthetic wastewater using different adsorbents such as anion exchange resin, non-ion exchange resin and GAC were studied in fixed-bed column. After finishing removal of PFOS and PFOA in column experiment, the adsorbents were regenerated by washing solvent technique. Preparations of adsorbents were conducted similar as in Section 4.3.2 and 4.3.3 in Chapter 4.

6.3.1 Fixed-bed column study for the removal of PFOS

Continuous removal of PFOS was performed by a fixed-bed column which was carried out using PP column. Inner diameter of column was 2 cm and length of the column was 30 cm. Column, PP tube, mesh, tank, and all equipment were rinsed with methanol and ultrapure water before starting the experiment. Mesh was put at top and bottom of column to prevent resin loss. Amount of adsorbent placed in each column was 20 cm^3. One column was run without adding adsorbent as a control unit. Column experimental set up is shown in **Fig. 6.1**. Before starting the experiment, methanol was fed into the column to avoid contamination of PFOS, and then followed with ultrapure water to remove dirt and remaining methanol. Each column was filled with ultrapure water for 24 hours to ensure all entrapped air bubbles in adsorbents were released.

The stock solution tank containing PFOS concentration of 105 μg/L was fed into mixing tank at a rate of 5 mL/min. Tap water was passed through GAC to remove chlorine residue and was pumped into mixing tank at 100 mL/min. Hence, PFOS concentration in mixing tank was 5 μg/L which was fed into each column at 15 mL/min. Effluent samples were collected every 3 days for measuring PFOS removal. There was a total of

122 operation days. Column experiments were terminated when the PFOS removal efficiency of all columns dropped to 90%. This experiment was conducted at 20 - 25°C, pH 7.1 and conductivity at 0.16 mS/cm.

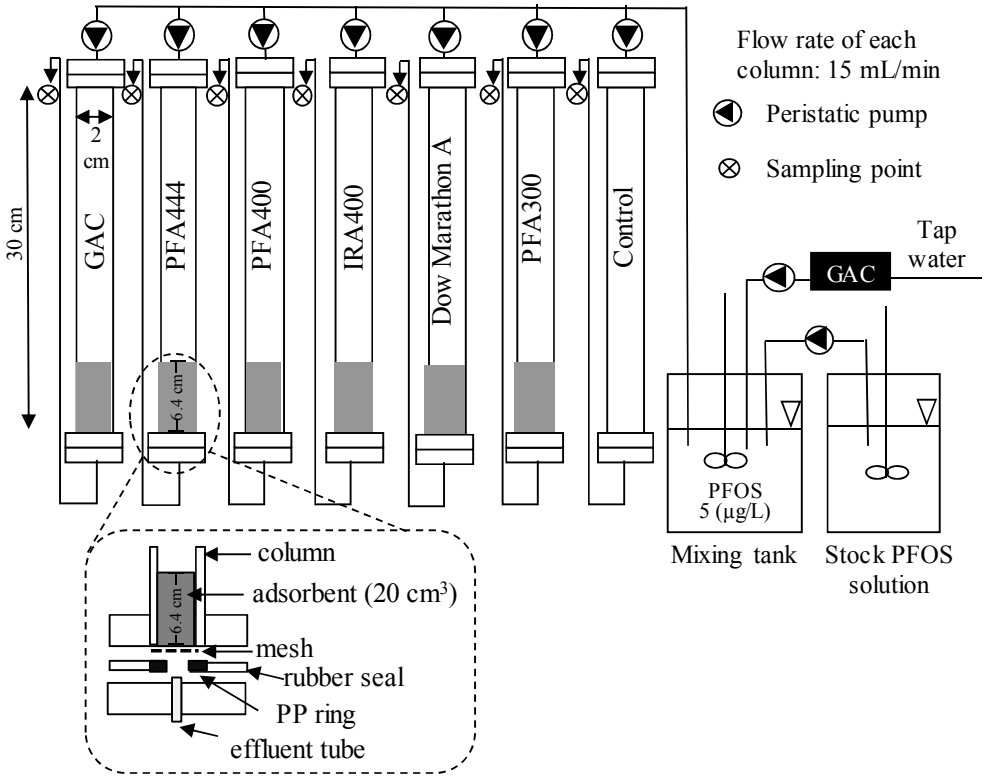


Figure 6.1 Schematic diagram of column experiment for PFOS removal

6.3.2 Fixed-bed column study for the removal of PFOA

Two anion exchange resins (PFA300 and Dow Marathon A) from previous experiment in section 6.3.2 were selected for removal of PFOA. XAD4 (non-ion exchange resin) was tested by a previous researcher in our lab that it showed high efficiency in PFOS removal (Senevirathna, 2010). Therefore, XAD4 was used to examine removal of PFOA. Additionally, GAC was examined because it was widely used in wastewater treatment process. Amount of adsorbent, flow rate and sample collection were set similar to PFOS removal experiment in Section 6.3.2. Column experimental set up for removal of PFOA

is shown in **Fig. 6.2** and photo of experiment set up is shown in **Fig 6.3**. The experimental of column condition is shown in **Table 6.1**.

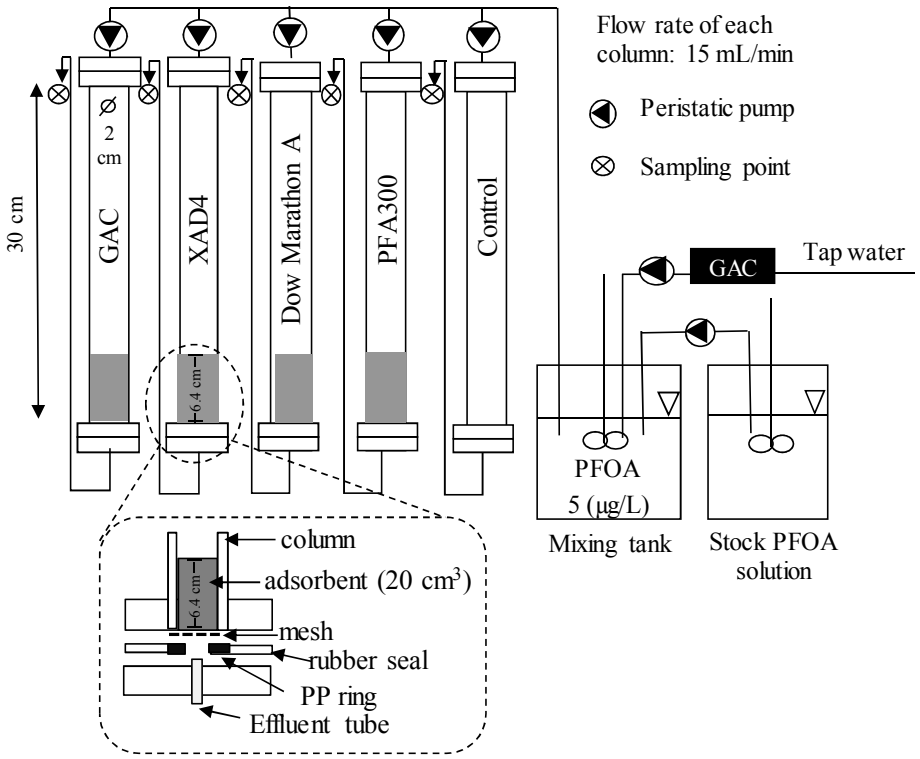


Figure 6.2 Schematic diagram of column experiment for PFOA removal

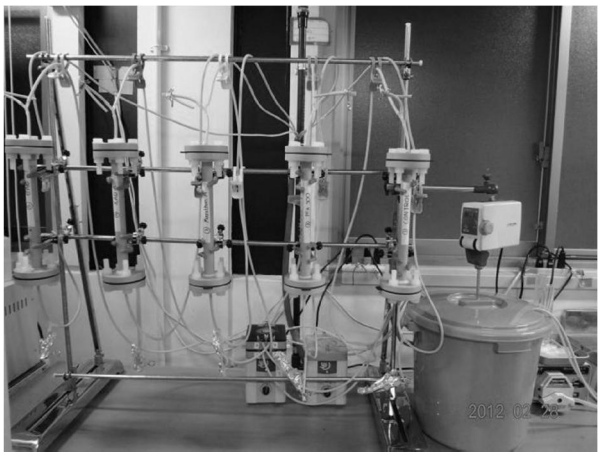


Figure 6.3 Photo of PFOA adsorption by column experiment

Table 6.1 Experimental conditions applied to the column experiments for PFOS and PFOA adsorptions

Parameters	PFOS Set value	PFOA Set value
Adsorbent	PFA300, PFA400, PFA444, IRA400, Dow Marathon A and GAC	PFA300 Dow Marathon A XAD 4 and GAC
Volume of adsorbent (20 cm^3)	20	20
Feed concentration (μg/L)	5	5
Flow rate in column (mL/min)	15	15
Retention time-column (min)	1.3	1.3
Temperature (°C)	20 - 25	15 - 20
Sampling time	Every three days	Every three days
Total operation days	122	117
pH in mixing tank	7.1	7.0
TOC in mixing tank (mg/L)	0.82	1.02
Conductivity in mixing tank (mS/cm)	0.16	0.16

Note: Retention time = Volume of adsorbent/flow rate

Previous researcher in our group (Senevirathna, 2010) conducted on removal of PFOS in column using only non-ion exchange resins (Dow V493, Dow L493 and XAD4) and GAC. Therefore, anion exchange resins (PFA300, PFA400, PFA444, IRA400 and Dow Marathon A) were focused on removal of PFOS in this study. In addition, there is no information on removal of PFOA in column. Therefore, anion exchange resin, non-ion exchange resin and GAC were tested for removal of PFOA.

6.3.3 PFOS and PFOA determination

Final effluent from each column (50 mL) was collected in PP tube every 3 days. PresepC-Agri (C_{18}) cartridge (Wako, Japan) was used to concentrate PFOS or PFOA in the samples. Cartridges were conditioned by 10 mL of methanol and 2 x 10 mL of ultrapure water before loading the sample into cartridges at 5 mL/min flow rate. They

were dried in manifold vacuum for 1.5 hours. Sample in dried cartridges were eluted by 2 x 2 mL methanol and 2 mL acetonitrile into PP tube. Eluted samples were completely dried by N_2 gas before being reconstituted by 1 mL of 40% acetonitrile in ultrapure water. Effluent concentration from each column was measured by HPLC-MS/MS.

6.3.4 Regeneration of used adsorbents after PFOS removal (batch experiments)

All adsorbents were taken out of the column and washed with ultrapure water. They were dried at 50ºC and homogenized by mixing. Each adsorbent (1 mg) was placed into 125 mL PP bottle which had been filled with 50 mL of regeneration solution. PFOS adsorbed onto resins were eluted by 5% NaCl in methanol/ultrapure water (7:3) while GAC was eluted by 100% methanol. They were shaken at 120 rpm and 25ºC. Samples were collected at varying intervals of time (1, 2, 4, 8 and 12 hours) and analyzed by HPLC-MS/MS.

6.3.5 Regeneration of used adsorbents after PFOA removal (column experiments)

Continuous removal of PFOA by column was stopped when all adsorbents reached a breakthrough point (90% removal efficiency). Experimental setup of regeneration is shown in **Fig. 6.4**. Before starting regeneration, column of PFA300 and Dow Marathon A were washed with ultrapure water (15 mL/min for 1 hour), methanol (5 mL/min for 1 hour) in order to remove non-adsorbed PFOA onto adsorbents and again with ultrapure water (15 mL/min for 1 hour) to remove remaining of methanol in column. However, XAD4 and GAC were washed with ultrapure water (15 mL/min for 3 hours). The regeneration was conducted by solvent washing technique. Adsorbed PFOA onto anion exchange resins (PFA300 and Dow Marathon A) were eluted by 5% NaCl in methanol/ultrapure water (7:3). Non-ion exchange resin (XAD4) and GAC were eluted by 100% methanol. Solution was fed into each column at 2 mL/min. Eluted samples were collected every 50 mL in PP tubes. Samples were diluted with 40% acetonitrile and were analyzed by HPLC-MS/MS.

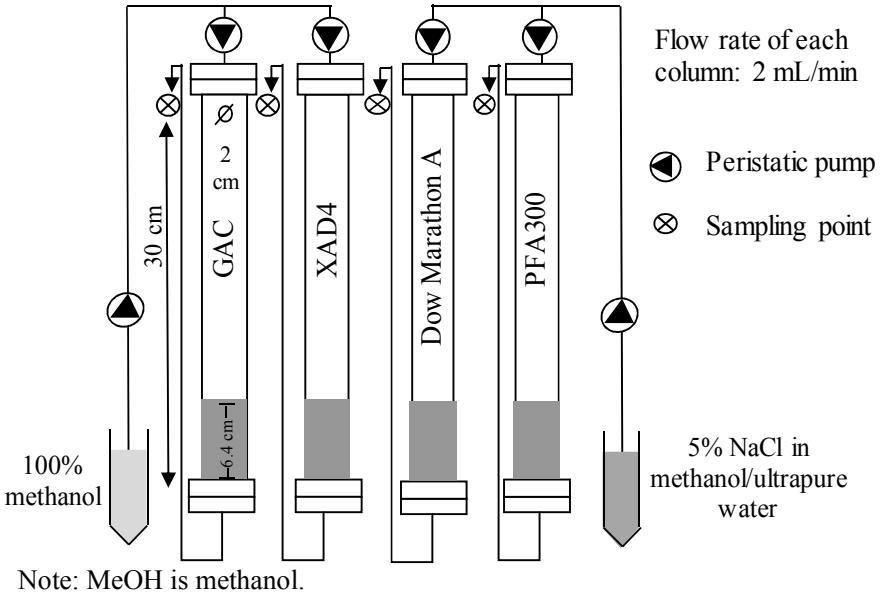


Figure 6.4 Experimental setup for adsorbents regeneration after PFOA removal

6.4 Results and discussion

6.4.1 Adsorption of PFOS onto anion exchange resin and GAC

Figure 6.5 shows the removal efficiencies of PFOS by six adsorbents against operation time. **Figure 6.6** shows PFOS in effluent concentration (µg/L) against No. of treated bed volumes. This experiment was carried out for 122 days to study the PFOS removal by adsorption of five ion exchange resins namely PFA300, PFA400, PFA444, Dow Marathon A, IRA400 and GAC. Relatively high flow rates were applied (15 mL/min) and 5 µg/L concentration of the PFOS feed solution was maintained providing a retention time of 1.3 min. Initial concentration was decreased to 5 µg/L in order to apply more practical conditions for the column experiment. The breakthrough point was set at 90% (C/C_o = 0.1) because PFOS usually presents in the water environment at the ng/L level.

The removal efficiencies of all adsorbents were more than 99% for 14 operation days (approximately 15,000 bed volumes). The removal efficiency was more than 90% for

PFA300 for a period of 118 days (127,440 bed volumes), Dow Marathon A for 109 days (117,720 bed volumes), IRA400 for 100 days (108,000 bed volumes), PFA400 for 91 days (98,280 bed volumes) and PFA444 for 76 days (82,080 bed volumes). PFA300 showed the better operational performance by removing more than 99% of PFOS for first 40 operation days (43,200 bed volumes passed through it). GAC showed the fastest breakthrough at 40 days. Senevirathna *et al*. (2010) reported that GAC was saturated at fast rate for PFOS removal. Thus, GAC filtration was ineffective to removal PFOS for long run operation.

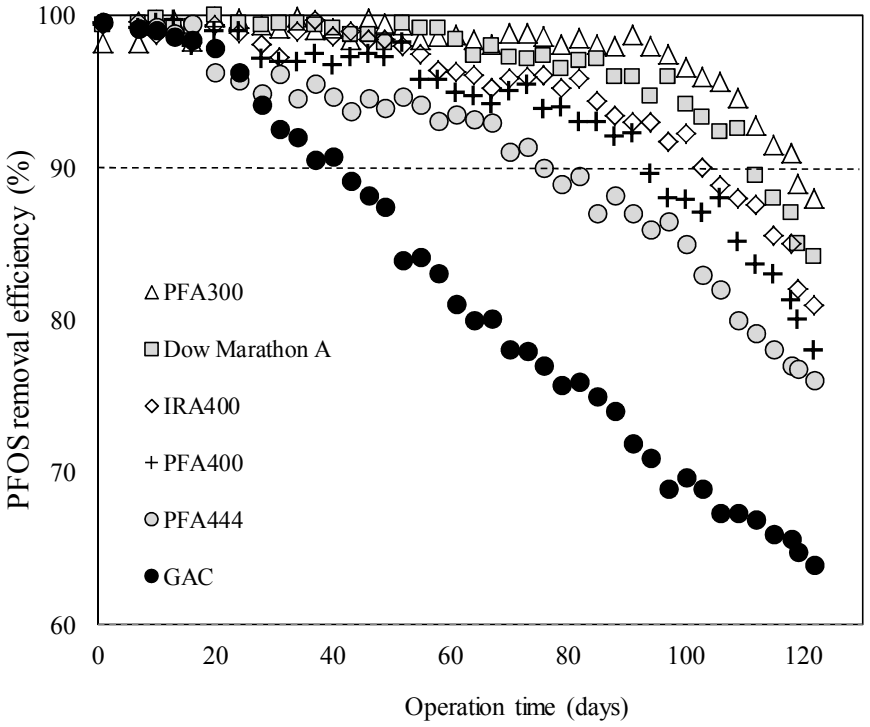


Figure 6.5 Removal efficiency of PFOS against operation time (122 days)

Longer operation days indicate that large volume of water can be treated as shown in **Fig. 6.6**. At breakthrough point (C/C_o = 0.1), the number of operating days decreased in order of PFA300 > Dow Marathon A > IRA400 > PFA400 > PFA444 and GAC, respectively. This result showed that anion exchange resins have higher removal efficiencies for the treatment of PFOS than GAC. Among five resins in this study,

PFA300 had the highest adsorption capacity of PFOS (455 mg/g) and also showed the better performance on the removal efficiency of PFOS in column experiment.

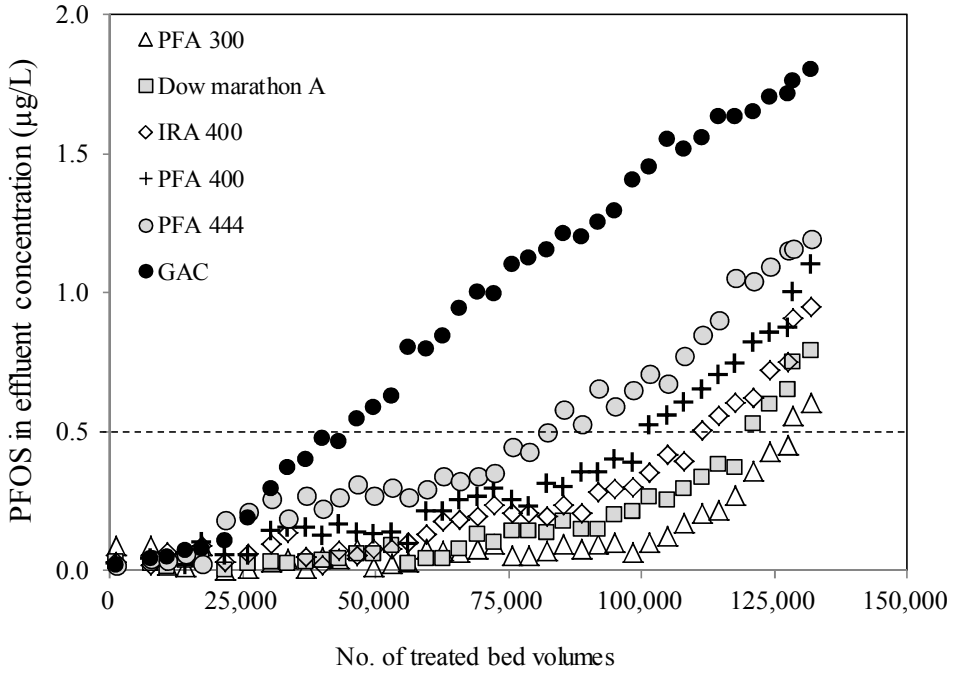


Figure 6.6 PFOS in effluent concentration (µg/L) against No. of treated bed volumes

Chemical and physical properties of resins are greater than GAC. In particular, resins have functional groups which can form chemical bonds with ions in the solution while GAC relies on physical interactions to remove contaminants from water (Flores *et al*., 2000). Resins generally have more controlled distribution of pore size than GAC. Moreover, resins have an extensive network of micropores which created high surface areas and abundant sorption sites.

Generally, the properties of anion exchange resins mainly differ in three aspects: polymer matrix, porosity, and functional group which not only influence the adsorption capacity, but also affect the adsorption rate. Strong base anion exchange resins can be categorized as type I and type II. Only PFA 300 is identified as type II (Table 4.1), which showed the highest removal efficiency of PFOS in this experiment. It has been

noticed that type II (R-$(CH_3)_2(C_2H_4OH)N^+$) had slightly greater capacity than type I. Hence, this functional group is more influential on PFOS adsorption.

6.4.2 Adsorption of PFOA onto anion exchange resin, non-ion exchange resin, and GAC

Figure 6.7 shows the removal efficiency of PFOA against operation time. Different kinds of adsorbents which, were anion exchange resin, non-ion exchange resin and GAC, were tested in this study. PFA300 and Dow Marathon A were selected from previous experiment (Section 6.4.1) which showed high performance on removal of PFOS. This experiment was set in similar conditions as in the PFOS removal by column. Breakthrough point was set at 90% removal efficiency of PFOA. It can be seen that the PFOA removal efficiency decreased in order of PFA300 > XAD4 > GAC > Dow Marathon A. PFA300 showed the better performance above 90% removal efficiency for 111 operation days while XAD4 was 60, GAC was 51 and Dow Marathon A was 30 operation days.

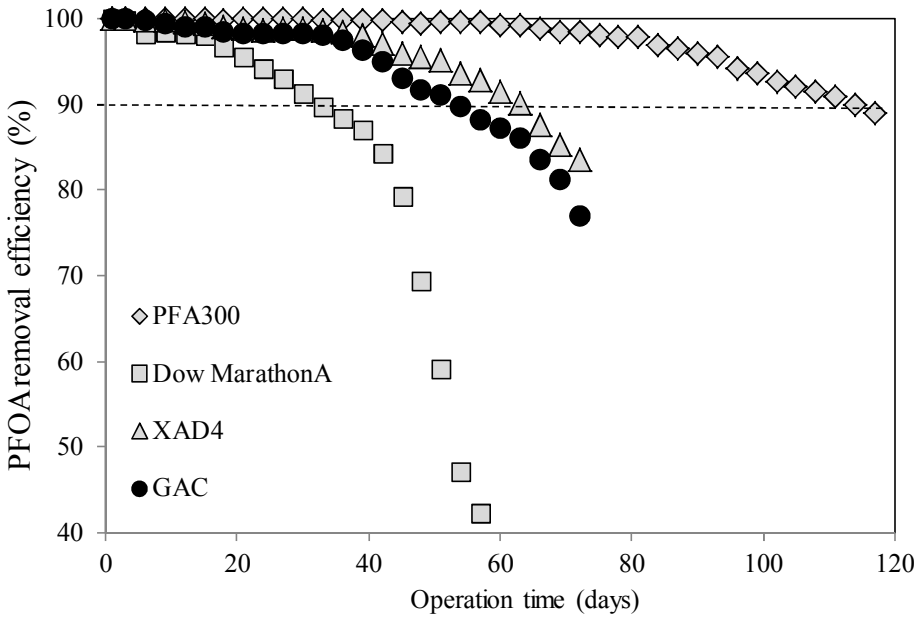


Figure 6.7 Removal efficiency of PFOA against operation time (117 days)

Figure 6.8 shows effluent PFOA concentration with No. of treated bed volumes. At approximately 99% of PFOA removal efficiency, PFA300 showed the highest No. of treated bed volumes (68,040 bed volumes). At 90% of breakthrough point, PFA300 showed the highest No. of treated bed volumes (119,880 bed volumes) followed by XAD4 (68,040 bed volumes), GAC (55,080 bed volumes) and Dow Marathon A (32,400 bed volumes), respectively.

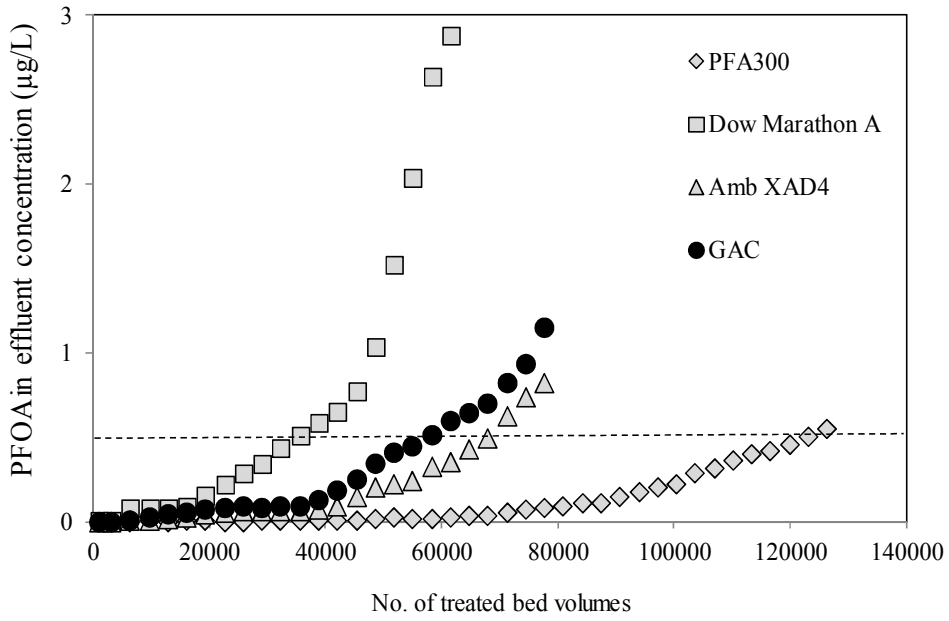


Figure 6.8 PFOA in effluent concentration (µg/L) against No. of treated bed volumes

Based on the results of PFOS and PFOA removal, it was found that PFA300 showed the better performance for removal of both PFOS and PFOA. Therefore, PFA300 is a suitable adsorbent which can be used instead of activated carbon and also the column technique can be applied for removal of PFCs in water/wastewater.

6.4.3 Regeneration of used adsorbents after PFOS adsorption

The regeneration was carried out by batch experiments. The total amount of PFOS adsorbed on adsorbents was calculated by integrating the area under **Fig. 6.5**. The

regeneration percentage was calculated using **Eq 5.1**. There were two types of solvents. First, 5% NaCl in methanol/ultrapure water (7:3) was used for anion exchange resins. Because PFOS had hydrophobic properties, solvent was mixed with methanol to increase solubility of PFOS. Second, 100% methanol was used for GAC.

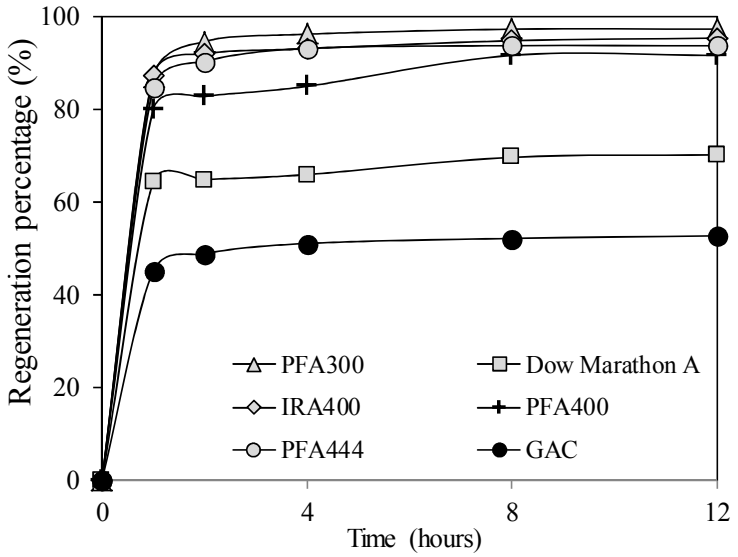


Figure 6.9 Regeneration percentages of used adsorbents from PFOS column

Figure 6.9 shows the regeneration percentage of used resins and GAC from column experiments. Most of anion exchange resins showed high regeneration percentage of PFOS of more than 93% except for Dow Marathon A (70%). PFA300 had the highest regeneration percentage, followed by IRA400, PFA444, PFA400, Dow Marathon A and GAC, respectively. Faster desorption of PFOS from anion exchange resins than from GAC was due to the interaction force between adsorbate and adsorbent. Adsorption of PFOS on GAC surface was due to stronger attraction than resins. The kinetic study in Chapter 4 showed that PFOS was adsorbed onto GAC at slow rate. When PFOS adsorbed in deep pores of GAC, it takes time to desorb PFOS into solvent. In general, resins are regenerated using chemicals, while the carbon is usually regenerated thermally because the adsorption forces are strong. Therefore, anion exchange resins are suitable adsorbents for PFOS removal in aqueous solution.

6.4.4 Regeneration of used adsorbents after PFOA adsorption

Although the previous section showed that adsorbents were regenerated by batch experiment, in real applications adsorbents are often regenerated onsite (in the column mode). Adsorbents which continuously adsorbed PFOA (Section 6.4.2) were suddenly regenerated in the column. Anion exchange resins (PFA300 and Dow Marathon A) were regenerated by 5% NaCl in methanol/ultrapure water (7:3) while XAD4 and GAC were regenerated by 100 % methanol.

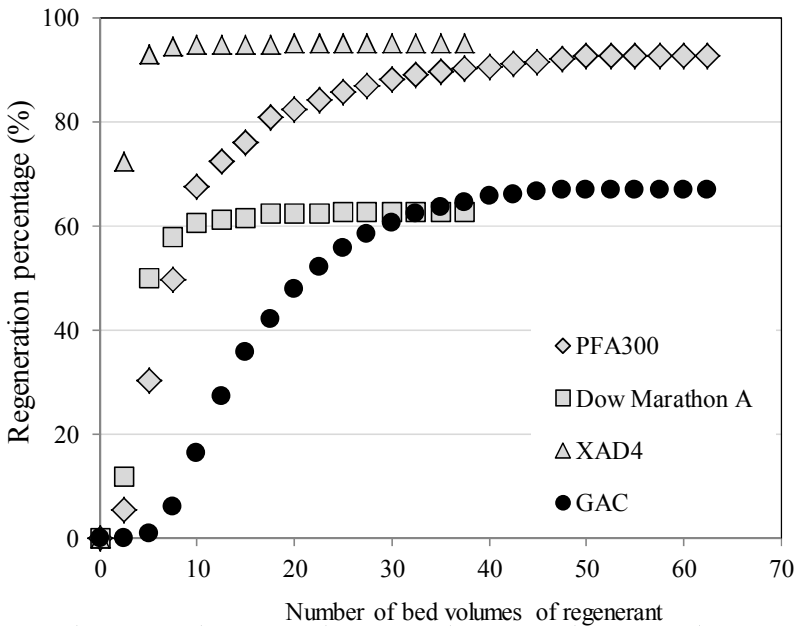


Figure 6.10 Regeneration percentages of used adsorbents from PFOA column

Figure 6.10 shows regeneration percentage of used adsorbents from column experiment. XAD4 showed the fastest regeneration above 90% at 5 bed volumes and reached to 95% at 17.5 bed volumes. PFA300 showed 93% of regeneration percentage at 55 bed volumes. GAC was 67% at 50 bed volumes and Dow Marathon A was 63% at 35 bed volumes. Non-ion exchange resins and anion exchange resins are manufactured through very similar processes. The main difference between the two resins is that anion exchange resins contain charged functional groups. Thus, this could be the reason for

faster desorption of PFOA from XAD4 than other adsorbents in this study. However, PFA300 had a high regeneration efficiency and high removal efficiency for PFOS and PFOA. Thus, PFA300 was suitable adsorbent for PFOS and PFOA removal and economical in terms of regeneration.

6.5 Cost benefit of regeneration technique

PFA300 was found to be an effective adsorbent for removal of PFOS and PFOA during longer operation days in column adsorption experiments and also was successfully regenerated using solvent washing technique. GAC is a common adsorbent used in water/wastewater treatment process. Regeneration of GAC is normally done at a separated (offside) using thermal technique. The regeneration cost was compared between solvent washing technique of resin and thermal regeneration of GAC. The cost analysis was based on column experiment on removal of PFOA in Section 6.4.2. **Table 6.2** shows the price of materials and chemicals for regeneration. The cost comparison of PFA300 and GAC regeneration is shown in **Table 6.3**.

Table 6.2 Supply price of materials and chemicals

Materials and chemical	Producers	Purchasing amount	Unit cost (Yen)
PFA300	Purolite Company	1 L	[a]2,000
GAC	Calgon Mitsubishi Chemical Company	1 kg	[b]17,000
Methanol	Wako Pure Chemical Industries	3 L	[b]3,700
NaCl	Wako Pure Chemical Industries	500 g	[b]2,700

Note: a. Personal communication with company
b. Laboratory suppliers

The objective of comparison of cost for regeneration of PFA 300 resin and GAC was to determine the cost saving by using PFA 300 for treatment of wastewater.

Table 6.3 Cost comparison for PFA300 and GAC regeneration

Materials	Operation conditions	Unit cost (Yen)	1st cycle (Yen)	2nd cycle (Yen)	3rd cycle (Yen)	4th cycle (Yen)	5th cycle (Yen)	6th cycle (Yen)
PFA300	20 cm^3	2/cm^3	40.0	-	-	-	-	-
Methanol	700 mL	1234/L	863.8	863.8	863.8	863.8	863.8	863.8
NaCl	62.5 g	5400/kg	337.5	337.5	337.5	337.5	337.5	337.5
Cost of regenerant	-	-	1241.3	1201.3	1201.3	1201.3	1201.3	1201.3
Total cost of PFA 300 regeneration	-	-	1281.3	1201.3	1201.3	1201.3	1201.3	1201.3
GAC	12 g	17000/kg	408.0	40.8	40.8	40.8	40.8	40.8
Cost of thermal regeneration of GAC	-	-	244.8	269.28	293.76	318.24	342.72	367.2
Cost of transportation of GAC	-	6299.0	6299.0	6299.0	6299.0	6299.0	6299.0	6299.0
Total cost of GAC regeneration	-	-	6543.8	6568.3	6592.8	6617.2	6641.7	6666.2

Assumptions for the cost comparison were as follows:

1. The cost analysis was based on the price of material supplied at the laboratory (Table 6.2).
2. PFA300 and GAC were considered for equal operation days *i.e*. 120 days and removal efficiency above 90%. As discussed in Section 6.4.2, the removal efficiency of GAC drops below 90% after 60 operation days, hence the amount of GAC was doubled for 120 operation days.
3. The cost of GAC regeneration was assumed to be 60% of price of GAC (Lambert *et al*., 2002)
4. During GAC regeneration, approximately 5 to 10 percent of the carbon are destroyed in the process or lost during transport (USEPA, 2000). Here, 10% loss was assumed and for every new cycle an additional cost for 1.2 g GAC was incurred.
5. Flat price for hiring a truck for transportation of GAC from laboratory to regeneration site was assumed.

6. In Chapter 5, PFA300 can be regenerated up to six cycles. Therefore, the cost of regeneration was calculated up to six cycles.

As shown in **Table 6.3**, the total cost of PFA300 and GAC regeneration for first cycle was 1,281 and 6,544 JPY respectively. The second to sixth regeneration cycle of PFA300 dropped to 1,201 JPY, while in case of GAC, it increased in every cycle due to loss of GAC during regeneration process and transportation. Therefore, use of PFA300 was much cheaper than GAC for wastewater treatment.

Moreover, the costs of methanol contributed to 69.5% of total cost of PFA300 regeneration. In this experiment, analytical grade materials were used. Therefore, the total cost of PFA300 regeneration will be much cheaper, if commercial grade materials will be used. Similarly, high proportion of total cost for GAC regeneration was due to transportation. If it is possible for onsite regeneration of GAC, then it will be cheaper than PFA300. However, PFA300 are much convenient to use than GAC.

6.5 Summary

Five anion exchange resins and GAC, which were studied by batch experiment in Chapter 4, were tested in column experiment for PFOS removal. For removal of PFOA, two anion exchange resins, non-ion exchange resin and GAC were used in column experiment. The conclusions of the experiment are summarized below.

1. PFA300 was recognized as the best adsorbent among the tested materials in this study to eliminate PFOS and PFOA.
2. At 90% removal efficiency, PFOS was continuously removed for 118 operation days while PFOA was continuously removed for 111 operation days by PFA300.
3. PFA300 showed high regeneration percentage for both PFOS and PFOA after finishing column experiments using 5% NaCl in methanol/ultrapure water (7:3) as regeneration solution. Solvent washing technique was approximately 5 times cheaper than thermal regeneration of GAC in each cycle.
4. The feasibility of column adsorption to removal PFOS and PFOA from real industrial wastewater was studied in Chapter 7.

Chapter 7

Application for industrial wastewater

7.1 Introduction

High concentrations of PFOS and PFOA were found in industrial wastewater. In 2009, the concentrations of PFOS and PFOA were detected from central industrial wastewater treatment plant in Thailand at 552.8 and 149.8 ng/L, respectively (Kunacheva *et al*., 2011). In 2012, different industrial wastewater in Thailand was detected 373.5 ng/L of PFOS concentration (Chapter 3). As the industries are the major source of PFOS and PFOA, the removal technique should be applied to minimize the impact of PFOS and PFOA at sources. Previous chapters showed that not only the adsorptions of PFCs by anion exchange resins were effective but also column experiments have shown the high percentage on removal of PFOS and PFOA. In addition, adsorbents also can be regenerated well as high potential for reusability. In this chapter, the column adsorption was applied in real wastewater to remove PFOS and PFOA for potential practical application.

7.2 Objectives

1. To study adsorption of PFOS and PFOA using anion exchange resin in industrial wastewater by batch experiments
2. To study suitable adsorbents for removal of PFOA in industrial wastewater by column experiments
3. To examine suitable flow rate for removal of PFOA in industrial wastewater
4. To examine suitable bed volume of adsorbent in the column
5. To investigate the removal of PFOS in industrial wastewater by using optimum column conditions

7.3 Methodology

7.3.1 Materials

Anion exchange resins (PFA300 and Dow Marathon A), non-ion exchange resin (XAD 4), and GAC were used in this study. Adsorbents were prepared in similar processes as Section 4.3.1 and 4.3.2 in Chapter 4.

7.3.2 Industrial wastewater preparation

a. Wastewater, which contained high concentration of PFBuS and PFOS, was collected from industrial WWTP in Thailand (IE5 in Chapter 3). The wastewater treatment processes are influent, primary clarifier, activated sludge, secondary clarifier, sand filtration, GAC filtration and effluent. In order to understand impact of wastewater quality on PFBuS and PFOS removal, wastewater from secondary clarifier and final effluent were collected and used for equilibrium adsorption and kinetics experiments. Moreover, final effluent was tested for removal of PFBuS and PFOS using column.

b. Another selected industry in this study deals with polytetrafluoroethylene (PTFE) which is located in Japan. PFTE is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The best known brand name of PTFE is Teflon. PFOA is a component used to manufacture PTFE, an ingredient in non-stick coatings. The wastewater treatment processes of selected industry included coagulation by PAC and biological treatment tanks. Final effluent, which contained high PFOA, was collected from industrial WWTP. Wastewater was filtered by 1 μm GF/B filter paper. Dissolved organic carbon (DOC) was expressed in term of total organic carbon (TOC) in filtrate. Initial TOC concentration was 15 mg/L and it was diluted with ultrapure water into 1 and 5 mg/L to study the effect of different TOC concentrations on removal of PFOA (batch experiments). PFOA was spiked in all samples to reach the initial concentration of PFOA at 600 ng/L. Next, the series of columns were installed at the final effluent of the WWTP before

discharging. Selection of adsorbents, flow rates and bed volumes were studied. TOC analyzer was used to measure the TOC content (in mg/L) of samples. The calibration curve of all TOC gave good coefficient of determination ($R^2 > 0.997$).

7.3.3 Batch experiments for adsorption of PFCs in industrial wastewater

Batch experiments were conducted by using the bottle-point technique. PFA300 was placed into PP bottles (125 mL) and 100 mL of wastewater was added. Experimental conditions were set as in **Table 7.1** and wastewater characteristics were showed in **Table 7.2**.

Table 7.1 Experimental conditions of batch experiments

PFCs	Wastewater	Experiments	Adsorbent	Amount of adsorbent (mg)	Shaking time (hrs)	Place
PFBuS and PFOS	Secondary clarifier Effluent	Isotherm	PFA300	1, 2, 4, 6, 8 and 10	96	Thailand
		Kinetic	PFA300	4	1, 3, 6, 12, 24, 48 and 72	
PFOA	Effluent	Effects of DOC	PFA300	4	1, 3, 6, 12, 24, 48, 72 and 96	Japan

Table 7.2 Industrial wastewater characteristics

Wastewater	PFCs concentration (ng/L)			DOC (mg/L)	Conductivity (mS/cm)	pH	SS (mg/L)
	PFBuS	PFOS	PFOA				
Secondary Clearifier	168	401	-	9.5	2.1	7.2	5
Effluent	156	373	-	6.7	2.0	7.3	ND
Effluent	-	-	600	15.0	0.5	7.5	ND

Note: Wastewater (200 mL) filters for SS.

After shaking, adsorbent was immediately separated by filtration (1 μm GF/B filter paper). Filtrated samples were loaded into PresepC-Agri (C_{18}) cartridges (Wako, Japan) connected inline with Oasis®HLB (Water, Japan). Both cartridges were conditioned with 10 mL of methanol and 2 x 10 mL of ultrapure water before loading the sample into cartridges at 5 mL/min flow rate. They were dried in manifold vacuum for 1.5 hours. Sample in dried cartridges were eluted by 2 x 2 mL methanol and 2 mL

acetonitrile into PP tube. Eluted samples were completely dried by N_2 gas before being reconstituted by 1 mL of 40% acetonitrile in ultrapure water. PFOS in effluent concentrations were periodically measured by HPLC-MS/MS.

7.3.4 Column experiments for PFOA removal

7.3.4.1 Selection adsorbent for PFOA removal

Four adsorbents were used in this study (two anion exchange resins (PFA300 and Dow Marathon A), one non-ion exchange resin (XAD4), and GAC). The five columns were installed at final discharge point of wastewater.

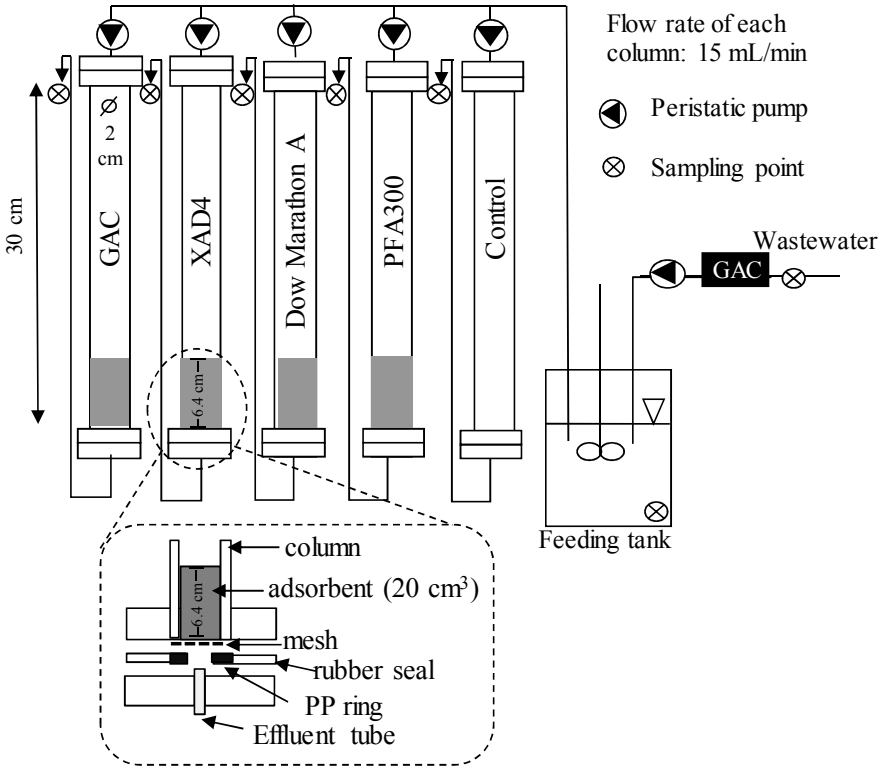


Figure 7.1 Experimental setup for selection of adsorbents for removal of PFOA in industrial wastewater

Effluent, which contained PFOA as major PFCs, was applied to study performance of each adsorbent in column mode. Adsorbents (20 cm^3) were placed into columns. The flow rate was 15 mL/min. The experimental setup is shown in **Fig. 7.1**. Samples were collected twice a week and experiments were continued until adsorbents were saturated. Samples pretreatment and analysis were done in a laboratory at Kyoto University

After that, PFA300 was washed with ultrapure water to remove dirt in the column and that was followed by methanol and again washed with ultrapure water. The 5% NaCl in methanol/ ultrapure water (7:3) was used for PFA300 regeneration (tested in Chapter 5). Regeneration solution was fed at 2 mL/min and eluent was collected every 50 mL for PFOA analysis. After regeneration, regenerated PFA300 was applied in Section 7.3.4.3 for reusability experiment.

7.3.4.2 Effects of flow rates

The best performing absorbent from Section 7.3.4.1 experiment was selected to study flow rate. Each column was fed at 5, 10, 15, and 20 mL/min of flow rates as shown in **Fig7.2**. One column was run in parallel as control and wastewater was fed at 15 mL/min.

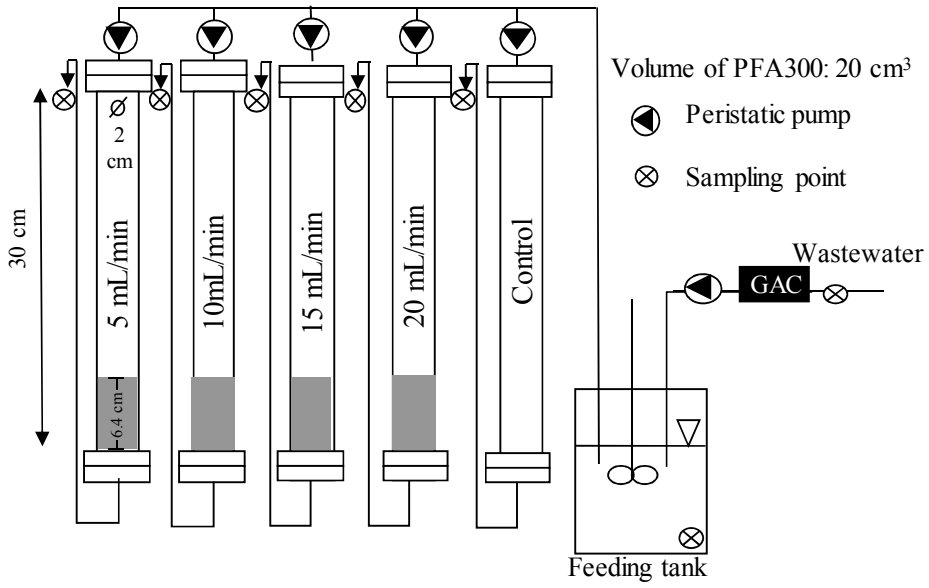


Figure 7.2 Experimental setup of different flow rates for removal of PFOA in industrial wastewater

7.3.4.3 Effects of bed volumes

Selected adsorbent (PFA300) and suitable flow rate were set for this experiment. There were three levels of bed volumes (10, 20, and 30 cm^3). Moreover, this experiment was conducted by controlling wastewater temperature at 35°C. In addition, reusability of regenerated resin from Section 7.3.4.1 was investigated in this experiment. **Figure 7.3** shows the experimental setup of different bed heights for removal of PFOA in industrial wastewater.

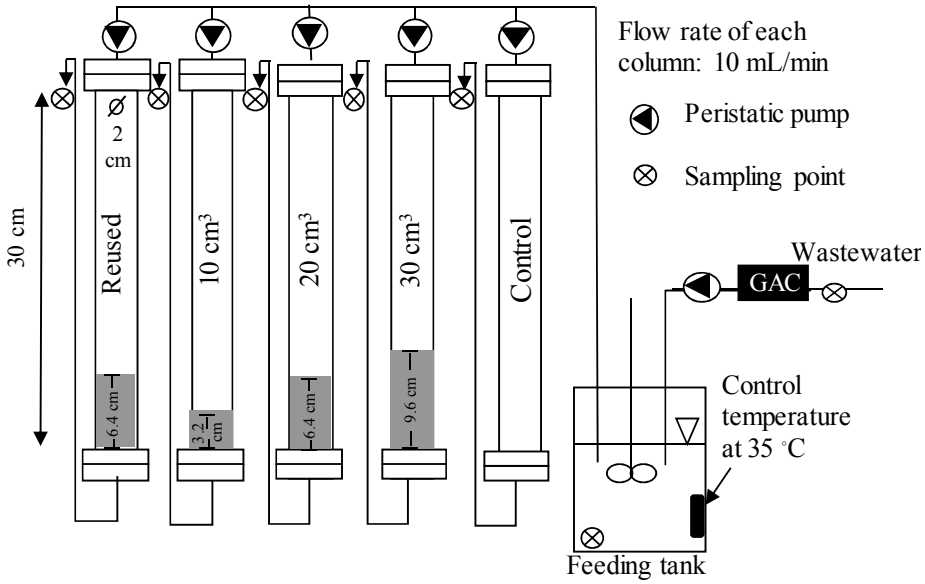


Figure 7.3 Experimental set up of different bed volumes for removal of PFOA in industrial wastewater

7.3.5 Column experiment for PFOS removal

The final effluent of industrial wastewater (IE5 in Chapter 3) was used and the experiment was conducted in Thailand. Continuous flow rate was performed by connecting of two similar columns for enhancing the removal efficiency of PFBuS and PFOS as shown in **Fig. 7.4**.

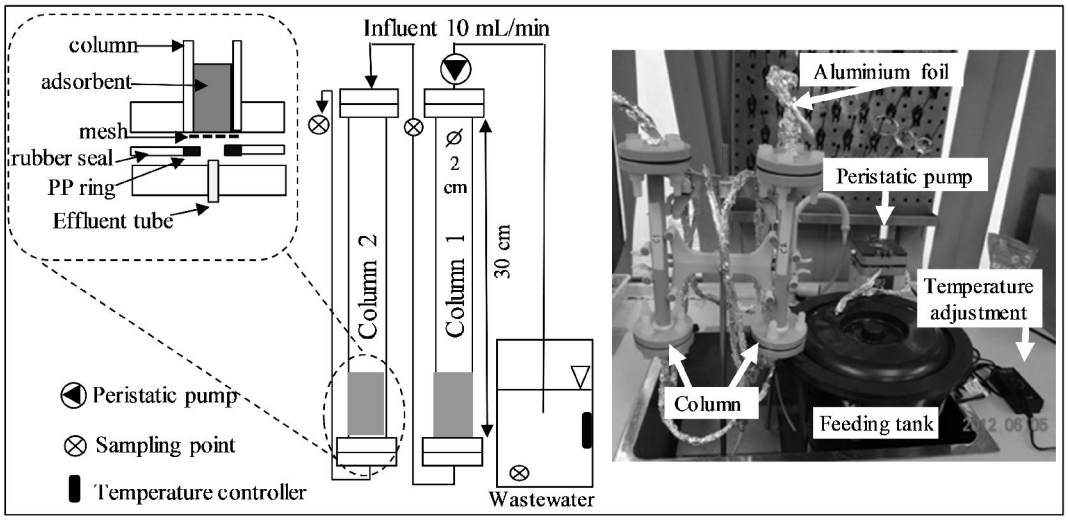


Figure 7.4 Experimental setup for PFBuS and PFOS removal from industrial wastewater

The major PFCs in industrial wastewater were PFBuS and PFOS. PFA300 (20 cm^3) was used as an adsorbent. The column was set similar as an optimum condition of PFOA removal in industrial wastewater from Section 7.3.4.1 to 7.3.4.3. Wastewater was controlled at 35°C and fed at 10 mL/min flow rate. Effluent samples of each column were collected every two days. Samples pretreatment were done in Thailand and kept in refrigerator at 4°C. Then, cartridges were brought back to Japan for further analysis.

Table 7.3 Summary of column experimental conditions in this study

Experiments	Target PFCs	Adsorbent	Amount of adsorbent (cm^3)	Flow rate (mL/min)	Remark
Selection of adsorbent	PFHxA, PFHpA and PFOA	PFA300, Dow Marathon A, XAD4, and GAC	20	15	PFA300 was regenerated.
Flow rate		PFA300	20	5, 10, 15 & 20	Effect of temperature
Bed height		PFA300	10, 20, and 30	10	Control temperature at 35°C & reusability of regenerated resin was studied.
Continuous flow	PFBuS and PFOS	PFA300	20	10	Control temperature at 35°C

Table 7.4 Industrial wastewater characteristics for each column experiment

Experiments	PFCs concentration (ng/L)					DOC (mg/L)	Conductivity (mS/cm)	pH
	PFHxA	PFHpA	PFOA	PFBuS	PFOS			
Selection of adsorbent	103	86	257	-	-	12.9	0.5	7.5
Flow rate	155	129	484	-	-	17.9	0.5	7.5
Bed volume	79	47	132	-	-	9.3	0.5	7.1
Continuous flow	-	-	-	182	478	7.2	2.1	7.7

7.4 Results and discussion

7.4.1 Adsorption of PFOS in industrial wastewater

In Chapter 3, it was shown that industrial wastewater had higher PFCs concentration than municipal wastewater. For the batch experiments, wastewater from IE5 was selected because it had the highest PFCs concentration in the final effluent. The wastewater treatment processes of IE5 were activated sludge, sand filtration and GAC filtration. Major PFCs in the effluent were PFBuS and PFOS. Batch experiments were conducted using both secondary clarifier and effluent as samples. DOC of 9.5 mg/L and 6.7 mg/L were observed in the secondary clarifier and effluent, respectively. Initial concentration PFBuS and PFOS in a secondary clarifier were 168 and 401 ng/L. In final effluent, PFBuS was 156 and PFOS was 373 ng/L.

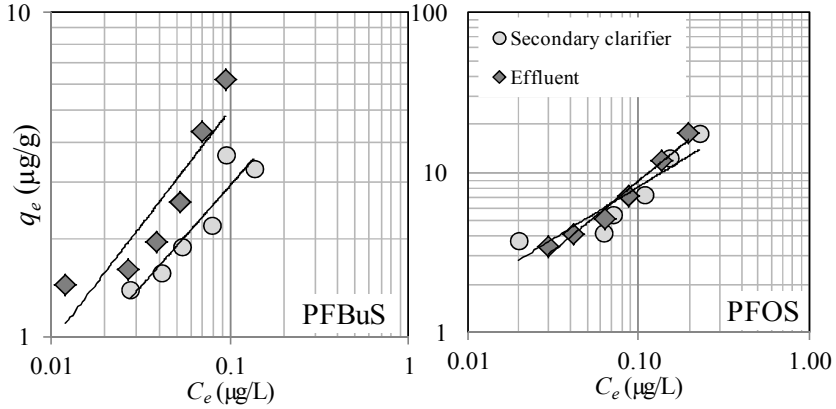


Figure 7.5 Adsorption isotherms of PFBuS and PFOS in industrial wastewater

The isotherm coefficient was determined in this study. **Figure 7.5** shows adsorption isotherm of PFBuS and PFOS in industrial wastewater onto PFA300. It showed that PFBuS and PFOS in effluent were easier to adsorb than in secondary clarifier.

Table 7.5 shows *Freundlich* isotherm constants for the adsorption of PFBuS and PFOS from secondary clarifier and effluent. K_f of PFOS was higher than PFBuS. PFOS has longer carbon chain and also more hydrophobic properties than PFBuS. Therefore, more absorption of PFOS onto PFA300 occurs through hydrophobic interaction. Additionally, K_f value in effluent was higher than in secondary clarifier. There were other compounds (matrix interferences) contained in secondary clarifier than in the effluent which might compete with PFBuS and PFOS and adsorb onto PFA300. This may be the reason for higher K_f of effluent than secondary clarifier.

Table 7.5 *Freundlich* isotherm constants for the adsorption of PFBuS and PFOS from secondary clarifier and effluent

PFCs	Wastewater	Freundlich isotherm paremeter		
		K_f	$1/n$	R^2
PFOS	Secondary clarifier	41.2	0.67	0.81
	Effluent	85.3	0.92	0.97
PFBuS	Secondary clarifier	12.3	0.62	0.87
	Effluent	26.0	0.72	0.82

7.4.2 Kinetics adsorption of PFBuS and PFOS in industrial wastewater

Figure 7.6 shows kinetics adsorption of PFBuS and PFOS onto PFA300 in secondary clarifier and effluent as well as effects of DOC and UV_{254}. PFOS was adsorbed faster onto PFA300 in secondary clarifier and effluent. This was due to the hydrophobic interaction mentioned in the previous chapter. PFBuS and PFOS in effluent have a higher removal efficiency than in secondary clarifier. Higher concentrations of other interferences such as DOC in secondary clearifier influenced adsorption of PFBuS and PFOS onto PFA300. DOC could be used to represent the level of organic carbon in water/wastewater. Tambo (1989) classified organic substances in DOC on the basis of

their ability to adsorb light in this UV range. He divided them into two fractions: UV-sensitive and UV-insensitive. McKnight *et al*. (1994) proposed the UV-sensitive fraction was mostly hydrophobic or aromatic in nature.

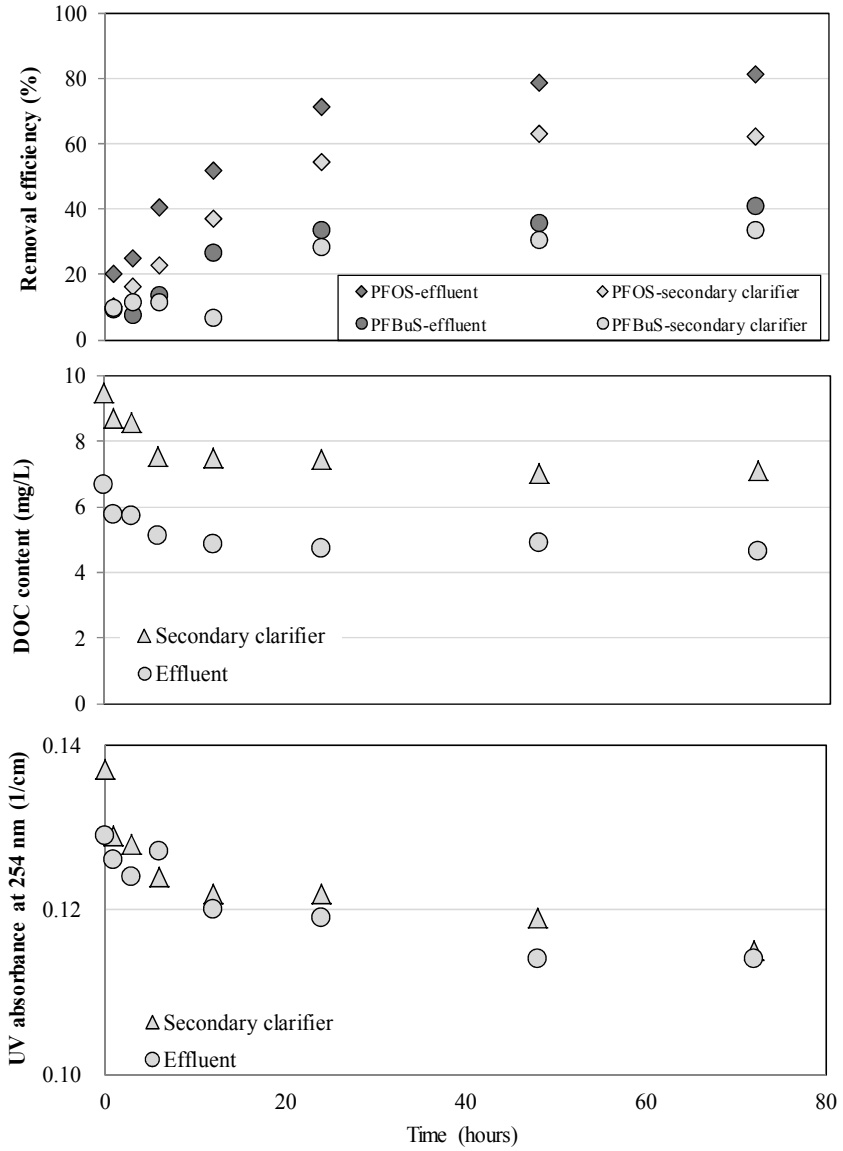


Figure 7.6 Kinetics adsorption of PFBuS and PFOS onto PFA300 in secondary clarifier and effluent and effects of DOC and UV_{254}

The adsorption of PFBuS and PFOS were affected by the DOC and hydrophobic or aromatic in wastewater because PFA300 did not only remove PFBuS and PFOS but also organic carbon contained in wastewater. Higher organic carbon contains in wastewater (secondary clarifier) are less efficient on removal of PFBuS and PFOS. Competitive adsorption between DOC and micropollutants depends on two major competitive mechanisms occurring: direct competition for adsorption sites and pore blockage (Pelekani and Snoeyink, 1999).

7.4.3 Influence of DOC on adsorption of PFOA in industrial wastewater

Figure 7.7 shows kinetic adsorption of PFOA onto PFA300 at different levels of DOC concentrations. DOC served as a parameter for quantifying bulk natural organic matter (NOM) concentrations. The experiment was conducted by using final effluent of industrial wastewater in Japan. Samples were prepared in different DOC concentration levels (1, 5 and 15 mg/L) using ultrapure water dilution. The result clearly showed a decrease of PFOA removal efficiency by increasing DOC concentrations in the samples.

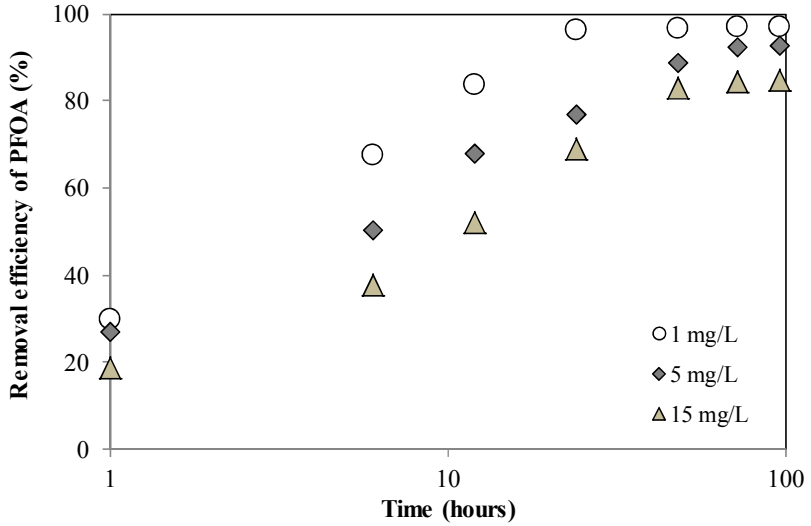


Figure 7.7 Kinetic adsorption of PFOA onto PFA300 at different levels of DOC concentrations

Competition between target trace compounds and NOM is common in adsorption processes, especially for drinking water treatment (Mardini and Legube, 2010). NOM has been shown to reduce the adsorption capacity of adsorbent for trace compounds typically present at concentration in the μg/L or ng/L levels. Researchers have identified direct site competition and pores blockage as the two primary mechanisms of competitive adsorption between trace compounds and NOM. The effects depended on the molecular weight distribution of the NOM as well as the pore size distribution and configuration of activated carbon pores (Li *et al*., 2003; Ding *et al*., 2006; Ding *et al*., 2008).

7.4.4 Column test for PFOA removal in industrial wastewater

7.4.4.1 Selection of adsorbents

PFCs concentrations in final effluent of industrial wastewater were measured. There were three major PFCs in wastewater, especially perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA) and perfluorooctanoic acid (PFOA). GAC was applied to filter the effluent in order to remove floc and particles in wastewater before feeding into columns. The initial concentration was 257 ng/L for PFOA. 103 ng/L for PFHxA, and 86 ng/L PFHpA.

Two anion exchange resins (PFA300 and Dow Marathon A), non-ion exchange resin (XAD4) and GAC were used to removal PFOA from industrial wastewater. The removal efficiency of each adsorbent is shown in **Fig. 7.8**. PFA300 showed highest removal efficiency followed by Dow MarathonA, XAD4 and GAC, respectively. At 20 operation days, PFA300 showed more than 80% removal efficiency of PFOA. PFOA removal efficiency of Dow Marathon A and XAD4 rapidly decreased after 6 operation days. Among four adsorbents, GAC was the least efficient absorbent to remove PFOA because it had the fastest saturation at 20 operation days.

Anion exchange resins presented higher removal efficiency of PFOA than non-ion exchange resin and GAC. Anion exchange resins were greater in terms of functional

groups which are specifically for removal of target compounds. Number of operation days was compared between removal of PFOA from synthetic wastewater (Chapter 6) and industrial wastewater. PFA300 used in synthetic wastewater took 117 operational days before efficiency dropped below 90% while it was only 14 operation days in industrial wastewater. There are a lot of interferences in wastewater which has higher concentrations (mg/L) than PFCs (ng/L). One major parameter is organic content in wastewater which influences several wastewater treatment techniques.

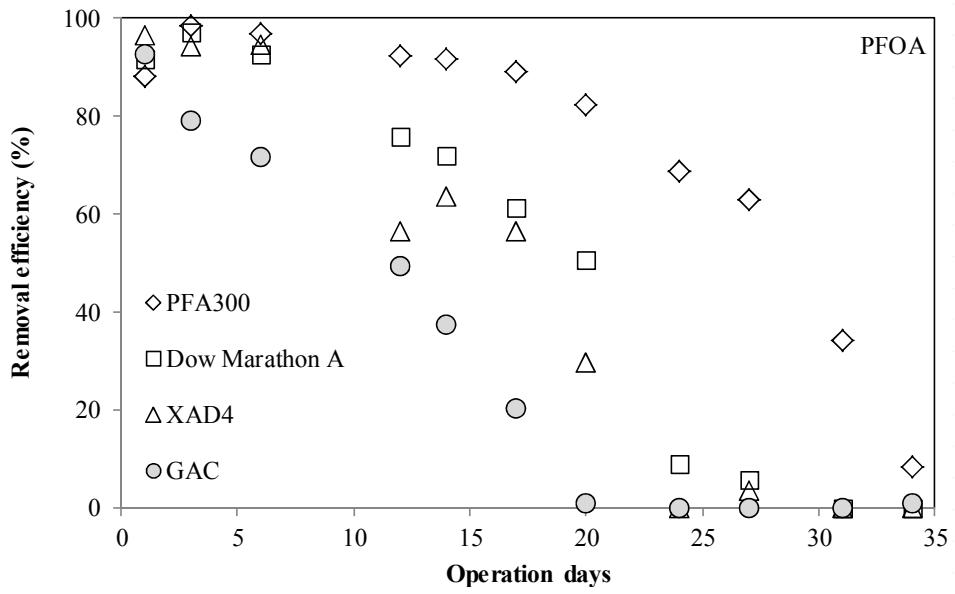


Figure 7.8 Continuous PFOA removal using, anion exchange resins, non-ion exchange resin and GAC

The adsorption performance of each adsorbent on removal of PFHxA, PFHpA and PFOA in industrial wastewater is shown in **Fig. 7.9**. XAD4 and GAC seemed to be ineffective to remove those PFCs in wastewater. However, all adsorbents showed similar pattern that long carbon chain PFCs were easier to remove than shorter ones. PFOA was well removed followed by PFHpA and PFHxA, respectively. Longer chain has more hydrophobic properties which enhance more adsorption onto adsorbents by hydrophobic interaction between sorbent and sorbate.

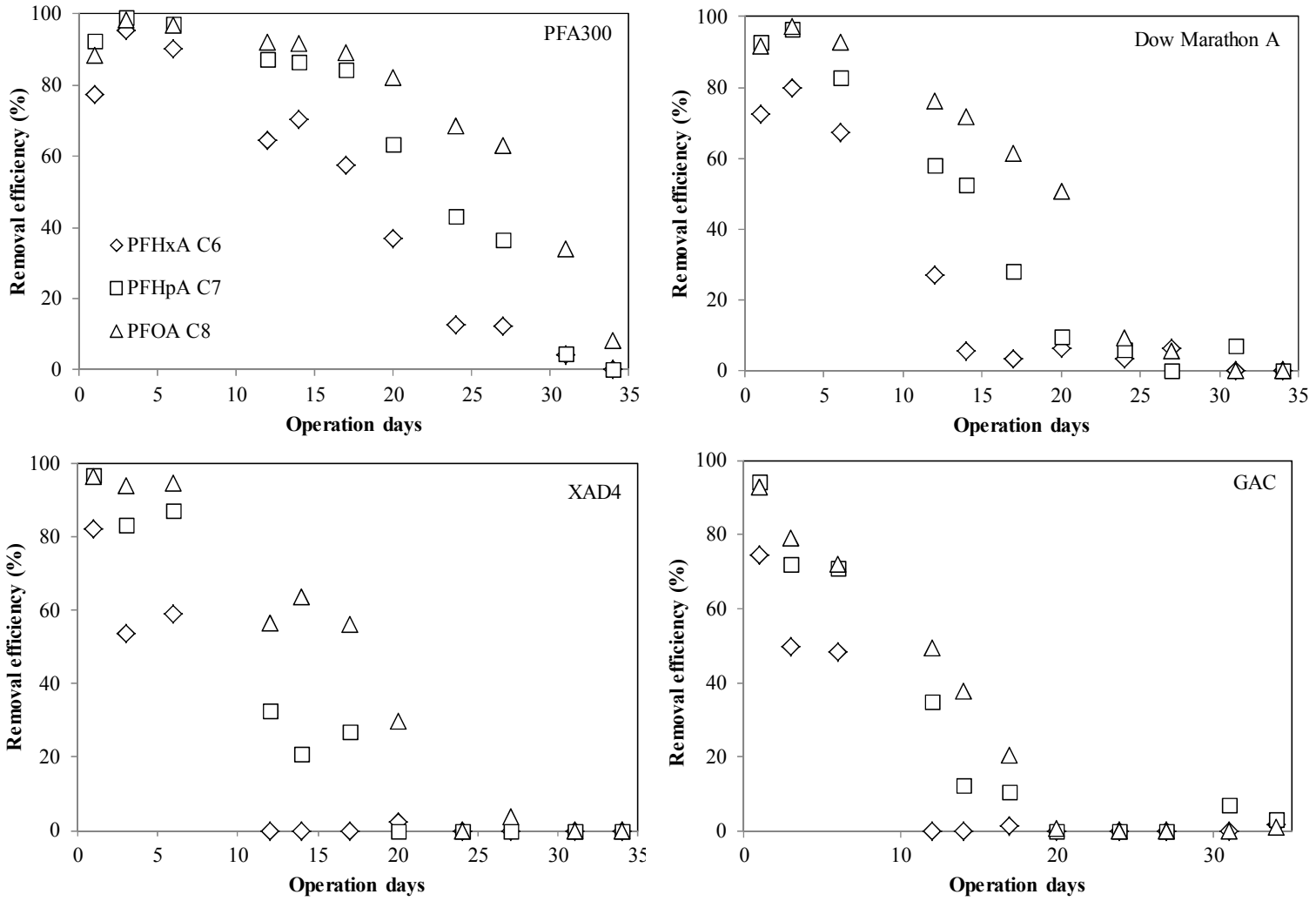


Figure 7.9 Adsorption efficiencies of each adsorbent on removal of PFHxA, PFHpA and PFOA in industrial wastewater

7.4.4.2 Regeneration of PFA300 used in removal of PFOA from industrial wastewater

PFA300 were selected for regeneration because it showed the highest removal efficiency in Section 7.4.4.1. After finishing PFOA removal experiment, PFA300 was immediately regenerated using solvent washing technique which was shown in Chapter 5. The 5% NaCl in methanol/ultrapure water (7:3) was applied for regeneration. Since, PFOA was the major PFCs in testing industrial wastewater, regeneration percentage was obtained from PFOA.

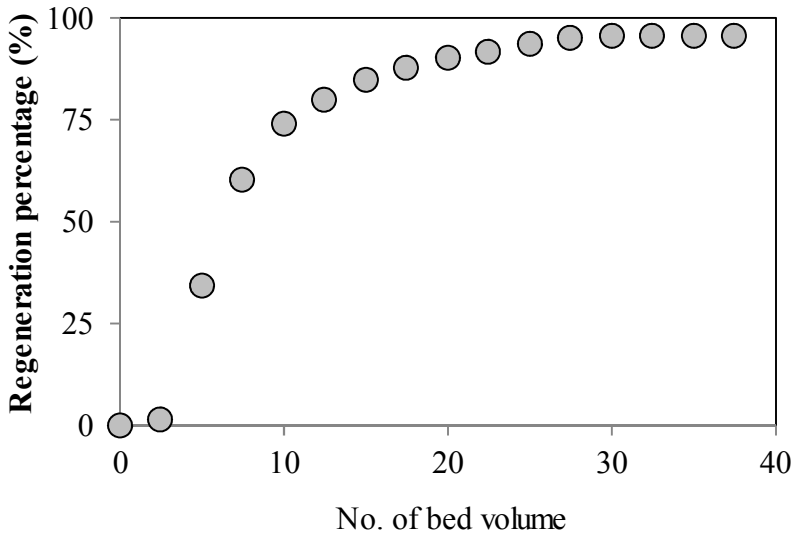


Figure 7.10 Regeneration percentages of used PFA300 in industrial wastewater

Figure 7.10 shows the regeneration percentage against bed volume of regeneration solution. PFOA was released when regeneration solution passed through PFA300. The maximum amount of PFOA released was 96% at 35 bed volumes (700 mL of 5% NaCl in methanol/ultrapure water (7:3)). In this study, PFA300 was the most effective adsorbent for removal of PFOA from industrial wastewater and also high regeneration efficiency. Next, the regenerated PFA300 was reused for removal of PFOA in industrial wastewater in the experiment of bed volume studies.

7.4.4.3 Selection of flow rates

Different flow rates (5, 10, 15, and 20 mL/min) were applied in this study using PFA300. Columns were stopped when removal efficiency of PFOA became less than 80%. Column performance was determined by plotting the removal efficiency of PFOA against operational days, as shown in **Fig. 7.11**.

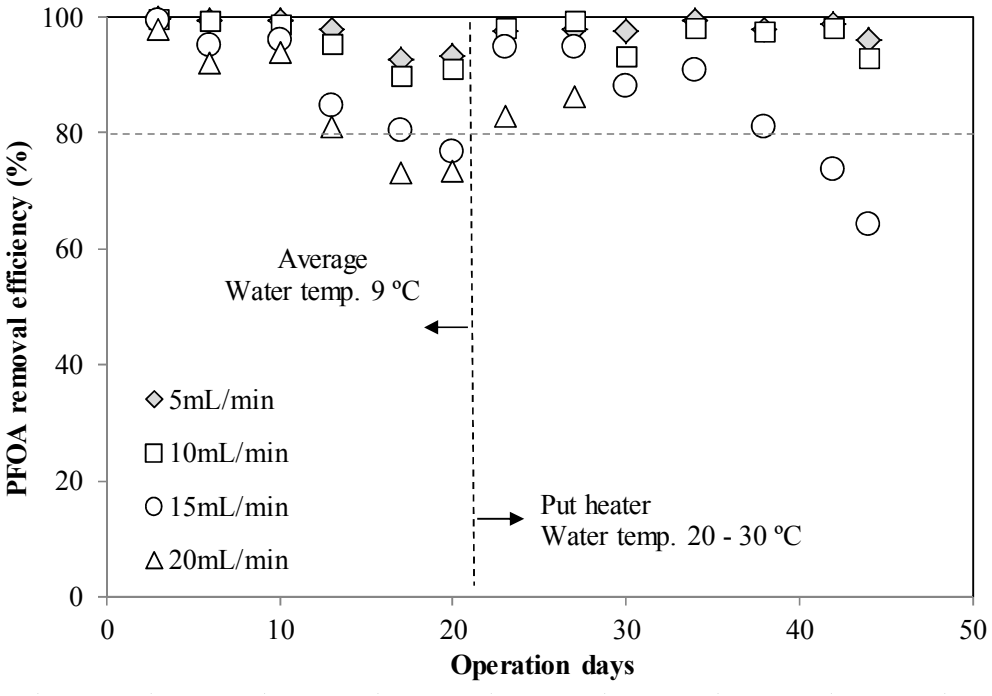


Figure 7.11 Removal efficiency of PFOA by PFA300 with different flow rates

The average initial PFOA concentration was 484 ng/L. The experiment was conducted on 13 January, 2012 in Japan. By 20 operational days, the PFOA removal efficiency of all flow rates dropped due to very low temperature (about 9°C) of wastewater. After 20 operation days, a heater was put into the storage tank because wastewater became frozen. The temperature was increased (20 – 30°C) which also increased the PFOA removal efficiency of all flow rates to higher than 80%. The effects of temperature were confirmed

by batch test in Chapter 4. Therefore, to enhance the removal efficiency of PFOA by column, the optimum wastewater temperature needs to be controlled.

The column performed well at lower flow rate (5 and 10 mL/min) while high flow rate exhausted the column at a faster rate. This was due to a decrease in the residence time, which restricted the contact of PFOA in wastewater to the PFA300. At higher flow rates the PFOA did not have enough time to diffuse into the pores of PFA300 and PFOA exited the column before equilibrium occurred.

Figure 7.12 shows the removal efficiency of PFHxA, PFHpA and PFOA in each column. PFOA was more adsorbed on PFA300 than PFHxA and PFHpA. The performance of 5 and 10 mL/min flow rates on removal of those three PFCs were not much different, especially the removal efficiency of PFOA which was higher than 93%. The higher flow rate indicates a larger amount of treated wastewater. Thus, 10 mL/min was selected for further experiment.

7.4.4.4 Effect of bed volume

In this experiment, PFA300 was used to adsorb PFOA with 10 mL/min of flow rate. Additionally, wastewater temperature was controlled at 35°C which showed high adsorbed PFOS and PFOA onto PFA300 in Chapter 4. Three different bed volumes were varied which were 10, 20 and 30 cm^3. **Figure 7.13** shows the effects of bed volumes on removal of PFOA. The average initial concentration of PFOA was 132 ng/L, lower than in previous experiments (Section 7.4.4.1 and 7.4.4.3). It can be seen that less volume of adsorbent (10 cm^3) shows slightly lower removal efficiency of PFOA than 20 and 30 cm^3 volume of adsorbent. The effect of bed volume was not clear in this test and this may be due to the low concentration of PFOA in wastewater and fewer operation days.

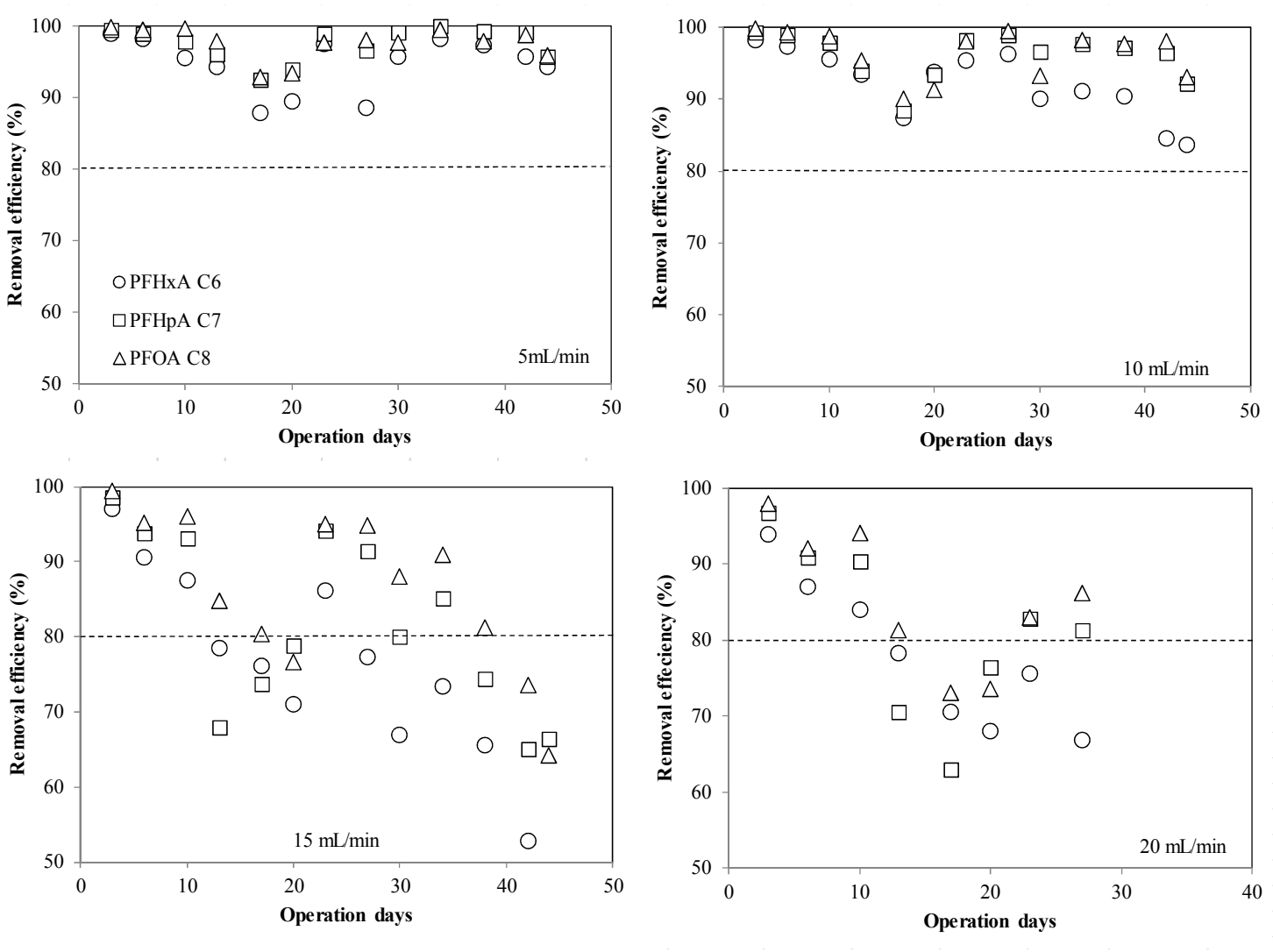


Figure 7.12 Removal efficiencies of PFHxA, PFHpA and PFOA with different flow rates

In general, binding sites were restricted at low bed volume where PFOA molecules did not have enough time to diffuse into the surface of adsorbent and reduction in breakthrough time occurs. Conversely, with an increase in bed volume, the residence time of PFOA inside the column was increased, allowing the PFOA molecules diffuse deeper into the resin.

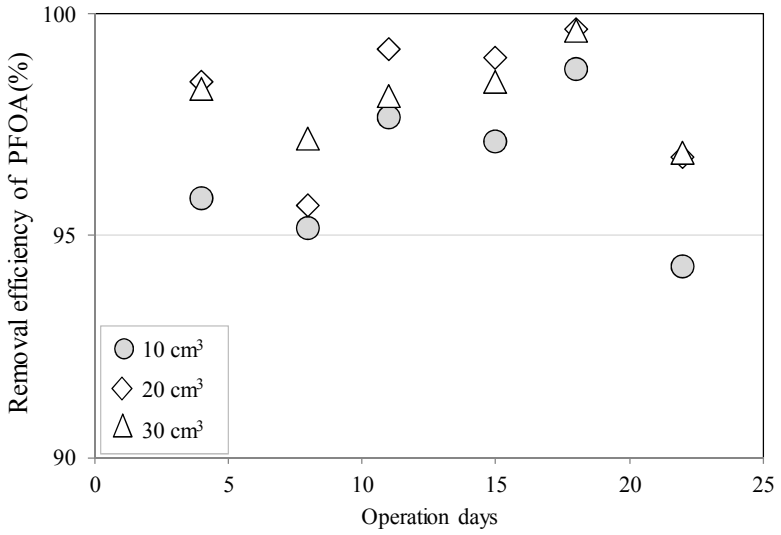


Figure 7.13 Removal efficiency of PFOA by PFA300 with different bed volumes

However, the results of 20 and 30 cm^3 bed volume were not much different in removal efficiency of PFOA. Therefore, 20 cm^3 was selected for the next experiment that was conducted in Thailand for PFBuS and PFOS removal.

7.4.4.5 Reusability potential of PFA300

Section 7.4.5.2 showed high regeneration efficiency of PFA300. After regeneration, PFA300 was reused for PFOA removal. The reusability study of PFA300 was conducted at the same period as the bed volume study and similar bed volumes were compared. **Figure 7.14** shows reusability of PFA300 on removal of PFOA in industrial wastewater in

comparison with fresh resin. Fresh and reused resins show almost similar results in removal efficiency of PFOA which can conclude that used resin still possesses high potential for PFOA removal after regeneration.

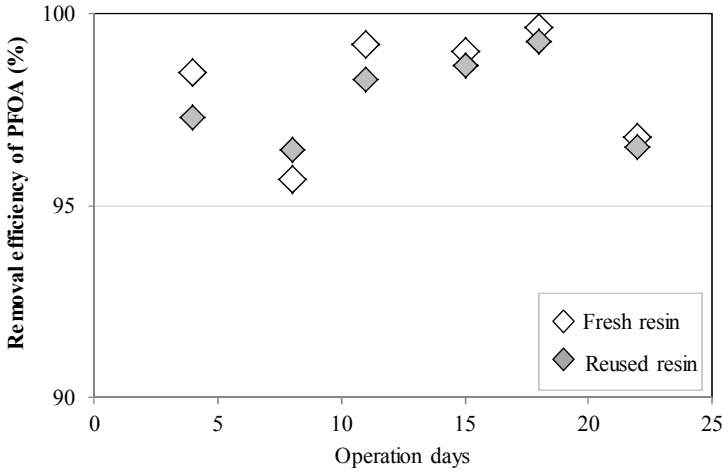


Figure 7.14 Reusability of PFA300 for removal of PFOA in industrial wastewater in comparison with fresh resin

7.4.5 Column test for PFOS removal in industrial wastewater

The continuous removal technique was also applied to industrial wastewater, which contains high concentration of PFBuS and PFOS. This study was conducted in June, 2012 in Thailand. The monitoring data found that industrial estate coded as IE5 (in Chapter 3) had the highest PFBuS and PFOS concentration. Thus, it was selected to apply column technique. The column was set at similar optimum conditions of removing PFOA in industrial wastewater which were determined in Japan. PFA300 was applied in column at 20 cm^3, 10 mL/min of flow rate and control temperature at 35°C. All tubes and connectors in this experiment were covered with aluminum foil and columns. In addition, they were kept in black house (covered with black plastic box) for protection from sunlight. The continuous flow adsorption experiment was conducted by connecting of two similar columns.

There were a total of 23 operational days. The average concentration of PFBuS was 182 ng/L and PFOS was 487 ng/L. Effluent wastewater was fed into a column for removal of those compounds. **Figure 7.15** shows the removal efficiency of PFBuS and PFOS after passing the first column. It was found that the removal efficiency of PFOS was more than PFBuS. At 10 operation days, the removal efficiency of PFOS was more than 99%. Then it slightly decreased to 97% at 23 operational days. Only 85% of PFBuS were removed in 23 operational days. In order to increase the removal efficiency of PFBuS the first column was connected to another similar column in continuous flow.

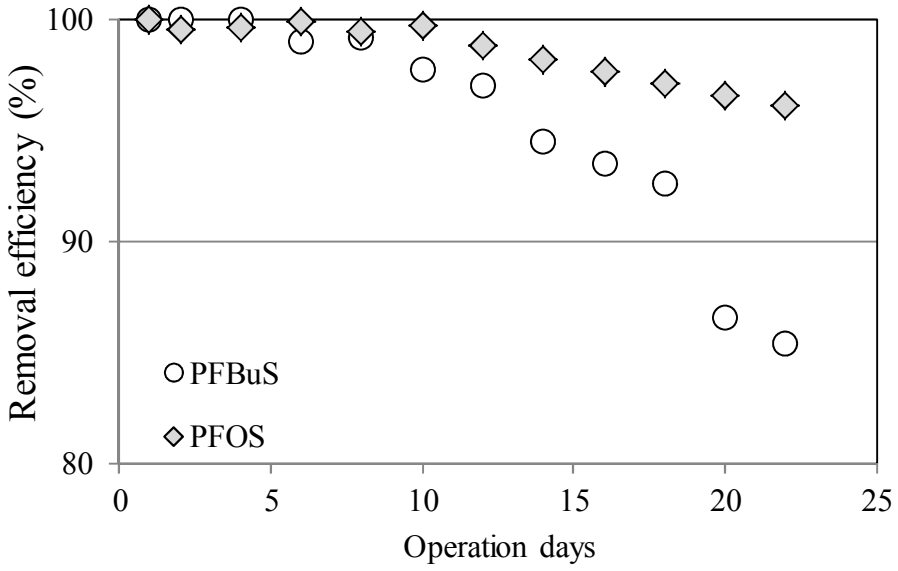


Figure 7.15 Removal efficiency of PFBuS and PFOS in industrial wastewater of first column

Figure 7.16 shows the overall removal efficiency of PFBuS and PFOS after wastewater passed through two columns. When wastewater passed through second column, PFBuS and PFOS showed removal efficiency of above 99%. In particular, the removal efficiency of PFBuS improved compared with column one.

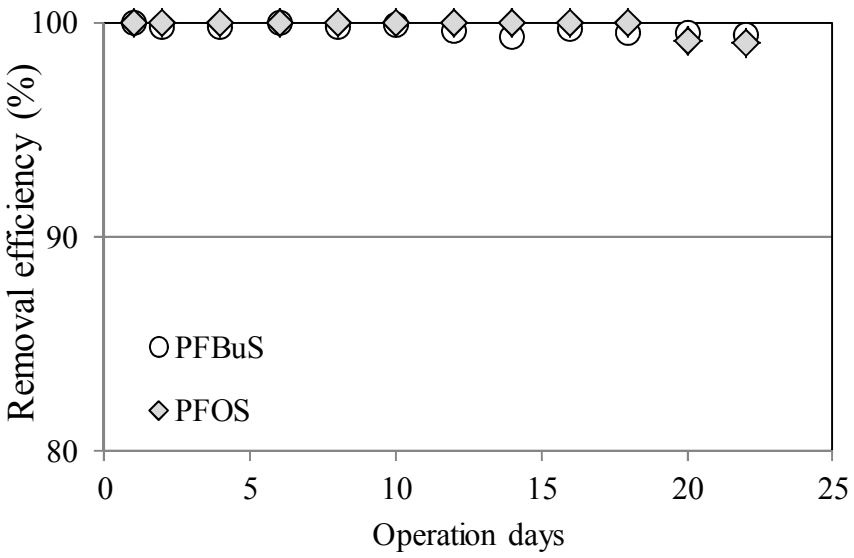


Figure 7.16 The Overall performance of removal efficiency of PFBuS and PFOS in industrial wastewater of continuous flow through two columns

7.5 Summary

In this chapter batch and column were applied in industrial wastewater. The conclusions of the experiment are summarized below.

1. Interferences in wastewater affected removal efficiency of PFOS and PFOA. There was reduction in adsorption capacity of adsorbent due to the high organic carbon concentration in wastewater.
2. PFA300 showed better performance than other tested materials for PFOA removal in industrial wastewater. In this study, suitable flow rate and bed volume for column adsorption were found to be 10 mL/min and 20 cm^3.
3. Two columns were connected which increased contacting time and available adsorption sites. Thus, removal efficiency of PFBuS and PFOS enhanced more than 99%.
4. Column adsorption technique was effective for removal of PFOS and PFOA from industrial wastewater and it can be scaled up for the real application.

Chapter 8

Conclusions and recommendations

8.1 Conclusions

PFCs are synthetic chemical compounds which are persistent, bio-accumulative and toxic chemicals and ubiquitously distributed in water, air, organisms and humans. Current wastewater treatment processes, especially activated sludge are ineffective to remove PFCs in trace levels. The suitable technology to treat low concentration level of PFCs in wastewater was developed in this research. The conclusions are drawn by chapters as follows.

Chapter 2 provided the available literature on PFCs basic information. Basic information of PFCs was introduced in physiochemical properties, persistent bio-accumulative and toxic properties, productions, applications, regulations, occurrences and removal techniques of PFCs.

Chapter 3 highlighted the performances of both MWWTPs and IWWTPs on removal of PFCs. Seven MWWTPs in Bangkok were studied. The highest of PFCs concentrations in effluent was found in Chong Nonsi followed by Jatujak, Nong Khaem, Din Daeng, Si Phraya, Rattanakosin and Throong Kru. PFOS and PFOA were predominant and their concentrations were high in both influent and effluent. In liquid and particulate phases, the PFCs concentrations in influents were almost similar in all MWWTPs which were lower than aeration, secondary clarifier, and final effluent. Long-chain PFCs were more adsorbed on particulate phase than short-chain ones. Moreover, industrial wastewaters from 5 IEs were investigated, which were found to have higher PFCs concentration than in MWWTPs. IE5 was detected the highest PFCs concentration in effluent. Thus, the effective removal technique of PFCs should be applied to industrial wastewater which was studied in next chapters.

Chapter 4 studied on the adsorption of PFCs by batch experiments. Anion exchange resins and GAC were used in this study for adsorption kinetics and isotherms. Anion exchange resins were more effective on removal of PFCs than GAC in both adsorption rate and capacity. PFA300 showed the better performance than other tested material in this study. When PFA300 was tested with eight single PFC, it showed that shorter chain of PFCs was more adsorbed than longer ones. However, mixed PFCs showed opposite result that long-chain PFCs (more hydrophobic properties) were more adsorbed than shorter ones. Temperature, pH and ionic strength influenced adsorption of PFCs onto PFA300. Based on the result of this study, PFA300 was the suitable adsorbent which can be used to remove PFCs in aqueous solution.

Chapter 5 studied on regeneration and reusability of used resin. PFA300 was selected because it had the highest of adsorption rate and capacity. Regeneration solution, regeneration rate and reusability were studied. PFA300 was successfully regenerated by NaOH and NaCl in methanol/ultrapure water (7:3). The solution of 5% NaCl in methanol/ultrapure water (7:3) showed the fastest regeneration rate. The reusability of regenerated PFA300 was high for PFOS removal for up to six cycles. PFA300 was the suitable adsorbent for PFCs removal because PFA300 has the highest adsorption capacity, high regeneration efficiency and high potential for reusability.

Chapter 6 studied on column experiment on removal of PFOS and PFOA. Resins and GAC were used in this study. Breakthrough was set at 90%. PFA300 was recognized as the best adsorbent among the tested materials to eliminate PFOS and PFOA. At 90% removal efficiency, PFOS was continuously removed for 118 operation days while PFOA was 111 operation days for PFA300. GAC showed poor performance on removal of both PFOS and PFOA. It can be suggested that use of anion exchange resins instead of GAC for removal of PFCs were more effective. Moreover, PFA300 also showed high regeneration percentage for both PFOS and PFOA after finishing column experiments.

Chapter 7 studied on application of removal technique in industrial wastewater by batch and column experiments. Batch tests found that matrix interference especially DOC in wastewater was affected by adsorption of PFOS and PFOA onto adsorbent. Column was installed at final effluent of IWWTP. PFA300 showed better performance than other tested material for PFOA removal in industrial wastewater. In comparison with column experiment in Chapter 6, the operation days were much different. Shorter operation days in industrial wastewater were due to interferences present in wastewater, which reduced adsorption capacity of adsorbent. Moreover, similar column conditions were applied to PFOS related industrial wastewater. It showed the high PFOS removal efficiency. When two columns were connected as continuous flow rate, the removal efficiency of PFBuS and PFOS were enhanced. Therefore, the column adsorption technique was successful in removal of both PFOS and PFOA in industrial wastewater.

8.2 Recommendations

The study results indicated PFCs contamination in MWWTPs and IWWTPs. Moreover, it was found that anion exchange resins were effective material for removal of PFCs in industrial wastewater when applied in column mode. The following are the recommendations.

1. PFCs adsorption was high in particulate phase. Sludge disposal/treatment needs to be investigated further.
2. Anion exchange resins were effective for PFCs removal, especially PFA300 which has type II functional group. However, further study with other type II resins should be done to confirm it. The percent of divinelybenzne in styrene polymer could cause size exclusion of PFCs into ion exchange sites. For better understanding the behavior of PFCs adsorption onto resin, effects of matrix types of resin (polystyrene and polyacrylic) and porosity types (gel and macroporous) are needed for further study.

3. The adsorption kinetic should be studied at different concentrations of PFCs to understand the effects of initial concentrations. Also, kinetic models such as pseudo-first-order, pseudo-second-order *etc*. are needed to be studied in order to investigate the controlling mechanism of adsorption processes, such as transfer and chemical reaction.
4. Buffer solution should be applied in adsorption experiments in order to avoid possibility of obtaining increased loadings of PFCs on the resins. In addition, resin can release hydroxide in order to avoid changing of pH solution. Therefore, buffer solution is needed and phosphate buffer is recommended.
5. Regeneration and reusability of resins used in industrial wastewater treatment should be further studied for the real application. In addition, different types of industrial wastewater are needed to understand the feasibility of regeneration solution as well as potential of reusability.
6. The regenerated solution will contain high concentration of PFCs. So, further treatments are needed.
7. GAC was generally regenerated by thermal technique, since PFCs strongly attached on GAC. The study on reusability of GAC regenerated by thermal technique is recommended.
8. Different type of wastewater may show different behavior of PFCs adsorption onto adsorbents. Thus wastewater characteristics need to be intensively studied to understand the effects of matrix interferences on adsorption of PFCs.
9. Combination processes (coagulation, chemical precipitation, UV, *etc*.) are recommended for removal of matrix interferences as well as for PFCs removal. The combined technique may maintain high removal efficiency at longer operation days.
10. More design parameters such as space velocity and linear velocity should be considered for scaling up of the column, so that similar removal efficiency in large column can be expected as in laboratory scale.

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Appendix A

Average PFCs concentration (ng/L) in liquid samples of MWWTPs

Date	WWTP	Sampling point	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHS	PFOS
19/10/2011	JJ	Influent	1.59	1.4	1.21	4.44	0.35	0.31	ND	ND	1.37	2.17	5.57
		Aeration tank	4.5	3.53	2.96	12.37	1.66	3.21	ND	ND	2.47	2.85	5.14
		Secondary clarifier	6.21	5.82	1.84	6.54	0.86	2.14	ND	ND	2.51	2.57	8.37
		Effluent	5.65	5.14	1.8	6.7	1.2	2.32	ND	ND	2.31	2.77	9.29
19/10/2011	DD	Influent	1.53	0.8	0.54	2.28	0.41	0.17	ND	ND	1.19	1.07	3.98
		Aeration tank	2.25	3.24	2.34	6.15	1.21	0.97	ND	ND	1.85	1.49	1.19
		Secondary clarifier	3.16	2.97	2.18	6.08	1.42	1.71	ND	ND	2.2	1.89	3.45
		Effluent	2.72	3.88	2.58	6.85	1.7	1.58	ND	ND	2.55	2.58	4.4
20/0/2011	RK	Influent	1.79	0.55	0.43	1.46	0.56	0.18	ND	ND	0.75	0.46	3.25
		Aeration tank	2.33	2.09	1.08	3.09	0.82	0.7	ND	ND	1.11	0.43	2.63
		Secondary clarifier	2.39	2.22	1.11	2.92	0.9	0.85	ND	ND	1.3	0.53	5.49
		Effluent	2.22	3.23	1.4	3.37	0.99	0.92	ND	ND	1.77	0.6	6.39
20/10/2011	SP	Influent	2.44	1.19	1.07	1.8	0.48	0.84	ND	ND	0.57	0.9	3.41
		Aeration tank	1.65	3.25	6.64	7.55	1.22	0.7	ND	ND	1.19	1.95	0.85
		Secondary clarifier	3.25	4.52	1.93	5.8	1.41	2	ND	ND	1.43	1.46	4.79
		Effluent	1.59	3.36	5.17	4.99	1.11	0.95	ND	ND	1.22	1.93	3.74
21/20/2011	CN	Influent	1.42	1	0.47	1.82	0.37	0.24	ND	ND	1.13	1.44	2.74
		Aeration tank	3.24	3.48	2.31	15.81	1.36	2.81	ND	ND	1.51	1.72	5.94
		Secondary clarifier	2.62	6.5	3.55	10.59	2.54	2.77	ND	< LOQ	2.71	2.74	7.45
		Effluent	1.29	4	6.78	6.88	6.42	5.28	4.71	4.2	6.47	8.46	9.03
21/10/2011	TK	Influent	1.69	0.93	0.9	2.14	0.51	0.24	ND	ND	0.98	1.02	3.8
		Aeration tank	2.78	2.11	0.78	4.37	1.6	1.44	ND	ND	0.4	1.17	4.42
		Secondary clarifier	8.25	4.35	2.16	6.09	1.54	1.99	ND	ND	1.71	1.46	7.79
		Effluent	2.78	2.52	0.78	2.21	0.36	0.76	ND	ND	0.4	0.2	2.64
25/10/2011	NK	Influent	2.08	1.48	1.82	5.4	0.94	0.36	ND	ND	1.02	1.33	3.53
		Aeration tank	4.27	3.2	2.92	8.17	1.65	1.28	ND	ND	1.15	1.24	3.58
		Secondary clarifier	5.26	4.04	2.69	7.73	1.56	2.13	ND	ND	1.48	1.16	6.13
		Effluent	4.41	4.19	2.89	7.36	1.64	1.74	ND	ND	1.38	1.2	4.74

Average PFCs concentration (ng/L) in solid samples of MWWTPs

Date	WWTP	Sampling point	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBuS	PFHS	PFOS
19/10/2011	JJ	Influent	0.15	1.19	0.23	0.46	0.13	0.19	0.00	0.00	0.00	0.00	1.47
		Aeration tank	2.67	4.73	0.92	3.78	1.59	10.65	2.45	9.54	0.00	0.00	41.47
		Secondary clarifier	0.16	1.09	0.20	0.32	0.00	0.07	0.01	0.00	0.00	0.00	2.85
		Effluent	0.15	1.56	0.20	0.40	0.00	0.20	0.15	0.00	0.00	0.00	1.33
19/10/2011	DD	Influent	0.50	0.91	0.30	0.50	0.12	0.09	0.02	0.00	0.00	0.00	0.31
		Aeration tank	0.98	2.16	0.10	0.59	0.00	4.32	1.62	7.39	0.00	0.00	13.55
		Secondary clarifier	0.14	0.89	0.39	0.57	0.07	0.47	0.05	0.07	0.05	0.00	1.75
		Effluent	0.77	2.07	0.63	0.66	0.18	0.69	0.08	0.13	0.00	0.00	1.94
20/0/2011	RK	Influent	0.12	1.14	0.38	0.54	0.00	0.01	0.00	0.00	0.00	0.00	0.84
		Aeration tank	0.24	0.03	0.09	0.55	0.00	2.74	1.64	6.52	0.21	0.00	55.80
		Secondary clarifier	0.21	0.80	0.29	0.26	0.00	0.11	0.02	0.07	0.00	0.00	3.16
		Effluent	0.33	2.08	0.53	0.31	0.00	0.06	0.02	0.00	0.00	0.00	2.77
20/10/2011	SP	Influent	0.54	0.90	0.16	1.60	0.00	0.06	0.00	0.00	0.00	0.00	1.22
		Aeration tank	0.25	0.04	0.76	2.52	0.46	10.66	4.18	24.21	0.00	0.82	43.99
		Secondary clarifier	0.24	1.87	0.83	0.43	0.00	0.12	0.03	0.03	0.00	0.00	2.63
		Effluent	0.49	1.19	0.26	0.32	0.00	0.17	0.26	0.00	0.00	0.00	0.72
21/20/2011	CN	Influent	0.21	1.19	0.28	0.56	0.07	0.11	0.16	0.46	0.00	0.00	0.57
		Aeration tank	0.07	0.00	0.21	1.87	0.45	11.29	4.41	16.23	0.00	0.07	46.60
		Secondary clarifier	0.24	1.01	0.21	0.91	0.00	0.39	0.10	0.25	0.00	0.00	2.15
		Effluent	0.14	0.74	0.17	0.37	0.00	0.06	0.02	0.00	0.00	0.00	0.45
21/10/2011	TK	Influent	0.48	3.52	1.03	0.31	0.00	0.00	0.00	0.00	0.01	0.00	0.40
		Aeration tank	1.47	3.42	1.61	10.14	2.18	21.56	8.42	25.27	0.00	0.29	63.42
		Secondary clarifier	0.18	1.40	0.40	0.50	0.00	0.12	0.04	0.00	0.00	0.00	2.04
		Effluent	0.18	1.28	0.29	0.47	0.01	0.09	0.00	0.00	0.00	0.00	1.93
25/10/2011	NK	Influent	0.22	1.85	0.26	0.57	0.19	0.14	0.02	0.02	0.91	0.00	0.50
		Aeration tank	0.41	0.79	0.32	1.85	0.21	5.01	1.87	4.62	0.00	0.00	18.64
		Secondary clarifier	0.21	1.54	0.21	0.36	0.07	0.11	0.07	0.00	0.00	0.00	0.94
		Effluent	0.16	0.97	0.16	0.38	0.03	0.12	0.07	0.00	0.26	0.00	0.99

Average PFCs concentration (ng/L) in tap water of each MWWTP

Date	WWTP	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHS	PFOS
19/10/2011	JJ	2.55	0.74	0.28	0.7	0.56	0.61	ND	ND	0.5	0.39	0.51
19/10/2011	DD	3.52	0.89	0.34	0.76	0.63	0.59	ND	ND	0.18	0.21	0.44
20/0/2011	RK	2.11	0.63	0.41	0.87	0.7	0.67	ND	ND	0.56	0.34	0.5
20/10/2011	SP	2.32	0.66	0.34	1.02	0.72	0.7	ND	ND	0.54	0.43	0.84
21/20/2011	CN	1.81	0.78	0.41	1.00	0.75	0.80	ND	ND	0.24	0.67	0.53
21/10/2011	TK	2.21	0.70	0.40	0.31	0.89	0.55	ND	ND	0.49	0.29	0.51
25/10/2011	NK	1.48	0.58	0.23	0.41	0.4	0.55	ND	ND	ND	0.88	0.42

Average PFCs concentration (ng/L) in liquid of IWWTP

Date	WWTP	Sampling point	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHS	PFOS
18/5/2012	IE1	Influent	12.86	5.91	2.88	19.25	4.53	2.18	ND	ND	39.52	<LOQ	15.19
		Effluent	15.40	13.00	11.30	36.50	11.50	3.10	ND	ND	48.90	ND	33.00
		Tap water	ND	0.70	0.10	0.30	<LOQ	1.80	ND	ND	ND	ND	0.30
22/5/2011	IE2	Influent	0.87	2.19	1.24	4.81	ND	2.34	<LOQ	ND	11.73	0.88	8.19
		Effluent	1.40	4.70	6.30	19.30	2.20	5.80	<LOQ	ND	23.20	3.20	11.50
		Tap water	ND	1.40	0.30	0.60	0.90	3.60	ND	ND	ND	ND	0.50
23/5/2012	IE3	Influent	1.28	0.76	1.62	2.16	1.54	ND	ND	ND	3.15	6.59	ND
		Effluent	4.00	2.50	2.90	6.60	3.40	1.10	ND	ND	20.00	16.00	6.30
		Tap water	2.20	1.70	0.40	1.50	1.00	<LOQ	ND	ND	ND	ND	0.70
24/5/2011	IE4	Influent	1.73	3.61	2.24	4.49	ND	2.19	ND	ND	71.06	0.94	1.77
		Effluent	31.80	10.90	18.80	40.80	ND	14.60	ND	ND	78.10	8.50	8.20
		Tap water	1.70	1.10	0.20	0.50	ND	2.20	ND	ND	ND	0.90	0.60
24/5/2011	IE5	Influent	<LOQ	5.06	5.08	14.95	15.56	<LOQ	ND	ND	202.97	37.72	315.48
		Effluent	10.00	16.70	35.60	8.90	22.40	<LOQ	ND	ND	156.30	37.40	373.50
		Tap water	0.20	0.30	0.30	0.70	0.80	0.10	ND	0.20	ND	1.90	0.80

Appendix B

Effects of temperature on the adsorption of PFOS and PFOA onto PFA300

Temperature	I	II	III	Avg. PFOS conc (μg/L)	Adsrobed PFOS (μg)	PFOS (mg/g)
10	240.3	249.4	239.1	242.9	75.7	15.1
20	113.2	115.1	120.0	116.1	88.4	17.7
30	49.2	44.9	44.8	46.3	95.4	19.1
35	17.8	18.1	18.0	17.9	98.2	19.6
40	11.3	14.3	11.2	12.3	98.8	19.8
45	21.0	23.2	23.2	22.5	97.8	19.6
50	33.6	31.0	28.1	30.9	96.9	19.4

Temperature	I	II	III	Avg. PFOA conc (μg/L)	Adsrobed PFOA (μg)	PFOA (mg/g)
10	329.2	337.9	321.6	329.6	67.0	13.4
20	141.0	143.5	144.5	143.0	85.7	17.1
30	62.4	64.8	62.1	63.1	93.7	18.7
35	20.5	19.8	20.6	20.3	98.0	19.6
40	18.0	19.0	18.4	18.5	98.2	19.6
45	23.6	22.2	23.6	23.1	97.7	19.5
50	33.6	31.0	28.1	30.9	96.9	19.4

Effects of pH on the adsorption of PFOS and PFOA onto PFA300

pH	I	II	III	Avg. PFOS conc (μg/L)	Adsrobed PFOS (μg)	PFOS (mg/g)
3	50.9	51.1	53.6	51.9	94.8	19.0
5	93.5	90.6	96.7	93.6	90.6	18.1
7	120.9	119.5	115.4	118.6	88.1	17.6
9	138.4	137.3	130.7	135.5	86.5	17.3
11	180.4	185.0	186.8	184.1	81.6	16.3

pH	I	II	III	Avg. PFOA conc (μg/L)	Adsrobed PFOA (μg)	PFOA (mg/g)
3	66.6	69.2	65.1	67.0	93.3	18.7
5	109.7	108.2	112.2	110.1	89.0	17.8
7	137.8	136.9	135.3	136.7	86.3	17.3
9	154.3	155.7	159.7	156.5	84.3	16.9
11	191.0	194.3	191.9	192.4	80.8	16.2

Effects of ionic strength on the adsorption of PFOA onto PFA300

NaCl (mM)	I	II	III	Avg. PFOA conc (μg/L)	AdsrobedPFOA (μg)	PFOA (mg/g)	Concutivity (mS/cm)
0.1	8.0	8.2	7.7	8.0	99.2	19.8	0.0
1.0	21.0	23.7	21.1	21.9	97.8	19.6	0.1
10.0	108.6	125.6	135.1	123.1	87.7	17.5	1.1
100.0	502.9	500.1	514.5	505.8	49.4	9.9	8.8
1000.0	847.7	825.0	848.2	840.3	16.0	3.2	57.0

Appendix C

PFOS removal efficiency (%) in synthetic wastewater (column experiments)

Days	1	7	10	13	16	20	24	28	31	34	37	40	43	46
PFA 300	98.2	98.3	99.7	99.7	98.3	99.9	99.8	99.4	99.2	99.9	99.0	99.1	98.4	99.8
Dow Marathon A	99.4	99.5	99.8	99.3	99.3	100.0	99.5	99.4	99.5	99.5	99.3	99.2	98.8	98.8
IRA 400	99.4	99.6	98.7	98.8	98.2	99.4	98.8	98.1	97.3	99.0	99.6	98.6	99.0	98.4
PFA 400	99.5	99.1	99.5	99.7	98.0	98.9	99.0	97.2	97.0	96.9	97.5	96.7	97.3	97.5
PFA 444	99.6	99.1	99.2	98.8	99.5	96.3	95.8	94.9	96.2	94.6	95.5	94.7	93.8	94.6
GAC	99.6	99.2	99.1	98.6	98.4	97.9	96.3	94.1	92.6	92.0	90.5	90.7	89.1	88.2

Days	49	52	55	58	61	64	67	70	73	76	79	82	85	88
PFA 300	99.5	99.3	98.4	98.6	98.7	98.5	98.1	98.9	98.9	98.6	98.1	98.5	98.1	98.0
Dow Marathon A	98.2	99.5	99.1	99.1	98.4	97.4	98.0	97.2	97.1	97.3	96.5	97.0	97.1	96.0
IRA 400	98.4	98.0	97.4	96.4	96.3	96.1	95.2	95.9	95.9	96.1	95.3	95.9	94.4	94.1
PFA 400	97.3	98.2	95.8	95.8	94.9	94.7	94.1	95.0	95.4	93.8	94.0	93.0	93.0	92.0
PFA 444	94.0	94.7	94.2	93.2	93.5	93.2	93.0	91.1	91.4	90.0	88.4	89.5	86.9	88.2
GAC	87.4	83.9	84.1	83.1	81.1	80.0	80.1	78.0	77.6	77.0	75.8	76.0	75.0	74.1

Days	91	94	97	100	103	106	109	112	115	118	119	122
PFA 300	98.7	98.0	97.5	96.7	95.9	95.7	94.6	92.8	91.5	91.0	88.9	88.0
Dow Marathon A	95.8	94.7	95.0	94.1	93.3	92.4	92.6	89.5	88.0	87.0	85.0	84.2
IRA 400	94.0	93.0	91.7	92.2	90.0	88.9	88.0	87.5	85.6	85.0	81.9	81.0
PFA 400	92.3	89.6	88.9	87.9	87.0	86.0	85.1	83.6	82.9	82.5	80.0	78.0
PFA 444	87.0	85.8	86.5	84.5	83.0	82.0	79.0	79.2	78.1	77.0	76.8	76.1
GAC	71.9	71.0	69.0	69.7	68.9	67.4	67.4	67.0	66.0	65.7	64.8	64.0

PFOA removal efficiency (%) in synthetic wastewater (column experiments)

Day	1	3	6	9	12	15	18	21	24	27	30	33	36	39
PFA300	100.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	99.9	99.9	99.9	99.9	99.9
Dow MarathonA	99.9	99.9	98.4	98.4	98.3	98.1	96.8	95.6	94.2	93.1	91.2	89.8	88.3	87.0
XAD4	100.0	100.0	99.9	99.8	99.7	99.5	99.2	98.9	98.7	98.8	98.8	98.7	98.5	98.2
GAC	100.0	100.0	99.9	99.4	99.1	99.0	98.6	98.4	98.3	98.4	98.2	98.2	97.5	96.3

Day	42	45	48	51	54	57	60	63	66	69	72	75	78	81
PFA300	99.8	99.7	99.5	99.6	99.6	99.6	99.3	99.3	98.9	98.5	98.4	98.2	97.9	97.8
Dow MarathonA	84.4	79.3	69.5	59.2	47.2	42.4	41.8	41.8	40.0	22.9	21.7	-	-	-
XAD4	97.0	96.0	95.6	95.2	93.5	92.9	91.5	90.2	87.6	85.3	83.5	-	-	-
GAC	95.0	93.1	91.8	91.1	89.7	88.2	87.2	86.0	83.6	81.2	77.1	-	-	-

Day	84	87	90	93	96	99	102	105	108	111	114	117
PFA300	97.0	96.6	96.0	95.5	94.2	93.7	92.7	92.0	91.6	90.8	90.0	89.0
Dow MarathonA	-	-	-	-	-	-	-	-	-	-	-	-
XAD4	-	-	-	-	-	-	-	-	-	-	-	-
GAC	-	-	-	-	-	-	-	-	-	-	-	-

Regeneration of adsorbent used in PFOS column experiment (Chapter 6)

Amount of PFOS adsorbed in column experiments

Adsorbents	Adsorbed PFOS (μg/mg)	1 mg in 50 mLof regenerant Maximum conc. (μg/L)
PFA300	0.93	18.6
Dow Marathon A	0.94	18.8
IRA400	0.87	17.4
PFA400	0.90	18.0
PFA444	0.88	17.6
GAC	0.91	18.2

PFOS conc. (μg/L) in interval sampling times

	PFOS conc. (μg/L) at different intervals						
Time (hrs)	0	1	2	4	8	12	24
PFA300	0	16.2	17.6	17.9	18.1	18.1	-
Mara	0	12.1	12.2	12.4	13.1	13.2	-
IRA400	0	15.2	16.0	16.2	16.5	16.6	-
PFA400	0	14.4	14.9	15.3	16.5	16.5	-
PFA444	0	14.9	15.9	16.4	16.5	16.5	-
GAC	0	8.2	8.9	9.3	9.5	9.6	9.61

Regeneration efficiency (%)

Time (hrs)	0	1	2	4	8	12	24
PFA300	0	87.1	94.6	96.2	97.3	97.3	-
Dow Marat	0	64.4	64.9	66.0	69.7	70.2	-
IRA400	0	87.4	92.0	93.1	94.8	95.4	-
PFA400	0	80.0	82.8	85.0	91.7	91.7	-
PFA444	0	84.7	90.3	93.2	93.8	93.8	-
GAC	0	45.1	48.9	51.1	52.2	52.7	52.8

Regeneration of adsorbent used in PFOA column experiments (Chapter 6)

Amount of desorbed PFOA (μg)

Amount of regenerant (mL)	0	50	100	150	200	250	300	350	400	450	500	550	600
No of bed volumn	0	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0
PFA300	0	700.0	3050.0	2400.0	2200.0	600.0	425.0	600.0	212.5	192.5	187.5	177.5	152.5
Dow MarathonA	0	725.0	2325.0	485.0	150.0	50.0	18.8	42.3	10.5	5.8	2.5	3.5	2.1
XAD4	0	5400.0	1550.0	100.0	25.0	4.9	10.0	1.9	1.0	0.6	0.8	0.6	0.9
GAC	0	9.0	74.8	365.0	750.0	792.5	625.0	470.0	420.0	300.0	262.5	207.5	150.0

Amount of desorbed PFOA (μg) (continue)

Amount of regenerant (mL)	650	700	750	800	850	900	950	1000	1050	1100	1150	1200	1250
No of bed volumn	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0	52.5	55.0	57.5	60.0	62.5
PFA300	112.5	66.0	59.5	58.7	56.4	44.5	64.6	68.3	16.0	5.4	1.4	1.3	0.3
Dow MarathonA	2.5	0.6	0.2	-	-	-	-	-	-	-	-	-	-
XAD4	0.6	0.3	1.0	-	-	-	-	-	-	-	-	-	-
GAC	137.5	95.0	70.5	71.0	33.1	32.5	20.6	9.9	1.3	0.8	0.2	0.1	0.1

Regeneration efficiency (%)

Amount of regenerant (mL)	Sum (μg)	Regeneration efficiency (%)
PFA300	11452.4	92.8
Dow MarathonA	3823.6	62.8
XAD4	7097.4	95.0
GAC	4898.9	67.0

Appendix D

Removal efficiency (%) of PFOA from industrial wastewater using PFA300, Dow Marathon A, XAD4 and GAC in column experiment

PFA300				
Date	Operation day	PFHxA	PFHpA	PFOA
181111	1	77.29	92.29	88.26
211111	3	95.37	98.92	98.43
241111	6	90.17	97.22	96.81
301111	12	64.62	87.05	92.18
21211	14	70.17	86.45	91.79
51211	17	57.50	84.18	89.07
81211	20	36.75	63.44	82.16
121211	24	12.69	43.07	68.60
151211	27	12.23	36.58	62.96
191211	31	4.10	4.43	34.06
221211	34	0.00	0.00	8.33

Dow MarathonA			
Operation day	PFHxA	PFHpA	PFOA
1	72.57	92.90	91.53
3	79.76	96.41	97.19
6	67.26	82.76	92.68
12	27.09	58.17	75.97
14	5.47	52.41	71.87
17	3.25	27.95	61.28
20	6.34	9.42	50.69
24	3.19	5.90	9.05
27	6.40	0.00	5.65
31	0.00	6.99	0.00
34	0.00	0.00	0.00

XAD4				
Date	Operation day	PFHxA	PFHpA	PFOA
181111	1	82.38	96.88	96.48
211111	3	53.83	83.20	94.19
241111	6	59.05	87.31	94.61
301111	12	0.00	32.75	56.44
21211	14	0.00	20.94	63.68
51211	17	0.00	26.99	56.36
81211	20	2.22	0.00	29.68
121211	24	0.00	0.00	0.00
151211	27	0.00	0.00	3.64
191211	31	0.00	0.00	0.00
221211	34	0.00	0.00	0.00

GAC			
Operation day	PFHxA	PFHpA	PFOA
1	74.33	94.32	92.75
3	49.75	71.84	79.14
6	48.18	70.81	71.79
12	0.00	34.93	49.46
14	0.00	12.24	37.56
17	1.24	10.65	20.43
20	0.00	0.00	0.77
24	0.00	0.00	0.00
27	0.00	0.00	0.00
31	0.00	7.03	0.00
34	1.59	3.04	0.98

Removal efficiency (%) of PFOA from industrial wastewater using PFA300 vary flow rate

Date	Operation days	5mL/min	10mL/min	15mL/min	20mLmin	Remark
16/1/2012	3	99.77	99.80	99.36	97.91	
19/1/2012	6	99.48	99.32	95.16	92.08	
23/1/2012	10	99.52	98.80	95.98	94.02	Average water temp. 9.4 °C
26/1/2012	13	97.75	95.44	84.76	81.21	
30/1/2012	17	92.75	89.99	80.44	73.08	
2/2/2012	20	93.40	91.32	76.70	73.56	
16/2/2012	23	97.68	98.11	94.94	83.04	water Temp. 21.6 °C Column stop on 2012/02/03 Column start on 2012/02/14
20/2/2012	27	98.02	99.37	94.87	86.14	water Temp. 21.8 °C
23/2/2012	30	97.73	93.26	88.03	Stop	water temp. 27.9 °C
27/2/2012	34	99.36	98.23	90.98	Stop	water temp 30 °C
1/3/2012	38	97.78	97.62	81.15	Stop	water temp 30 °C
6/3/2012	42	98.79	98.09	73.60	Stop	water temp 35 °C
8/3/2012	44	95.92	93.05	64.30	Stop	water temp 35 °C
12/3/2012	48	96.22	Stop	Stop	Stop	water temp 21 °C

Remval efficiency (%) of PFOA from industrail wastewater using PFA300 vary bed volume

Date	Operatin days	10 cm^3	20 cm^3	30 cm^3	Reuse (20cm^3)
7/12/2012	4	95.84	98.47	98.31	97.28
7/16/2012	8	95.19	95.70	97.21	96.47
7/19/2012	11	97.69	99.22	98.14	98.30
7/23/2012	15	97.14	99.01	98.46	98.66
7/26/2012	18	98.76	99.66	99.64	99.26
7/30/2012	22	94.30	96.77	96.86	96.52